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Enhancement of Pt Utilization in Electrocatalysts by Using Gold Nanoparticles**

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Many important reactions are strongly dependent on noble-metal catalysts, such as electrochemical reactions on the Pt electrode in proton-exchange membrane fuel cells (PEMFC).[1] The development of this promising application has been hampered because of the high cost of the catalyst.[2,3] One way to lower costs is to make the most efficient use of the noble metals so that every metal atom is used in the catalytic process. Because catalysis at the electrode of a fuel cell is a surface phenomenon, the utilization of Pt in electrocatalysts can be defined as the dispersion or exposed percentage of Pt atoms in the catalyst, which is approximately equal to the reciprocal of the Pt particle size in nanometers.[4,5] According to a number of recent reports, the most favorable particle size for Pt-based electrocatalysts is in the range of 2–4 nm.[6–9] Therefore, the utilization or exposed percentage of Pt atoms in these state-of-the-art electrocatalysts is in the range of 25–50%, far below a 100% utilization or dispersion of the ideal model. To enhance Pt utilization, it would be necessary to further decrease the particle size of Pt-based electrocatalysts.

A reasonable expectation would be that for Pt particle sizes of about 1 nm or smaller a 100% Pt utilization in electrocatalysts could be theoretically possible. In practice, however, metal particles smaller than 2 nm are readily pocketed by the micropores (≤ 2.0 nm) of the conductive carbon supporting material and consequently become inaccessible for electrochemical reactions,[10–12] which leads to a significant lowering of the overall Pt utilization. Furthermore, the behavior of very small metal particles (ca. 1.0 nm or smaller) would deviate significantly from that of metallic particles owing to their strong interaction with the surface of the supporting material.[13–15] Therefore, it is important to seek alternative approaches for enhancing Pt utilization in carbon-supported electrocatalysts.

Herein, we present a method to enhance Pt utilization in Pt/C-based electrocatalysts by using Au nanoparticles to support the Pt. Gold is chosen because it is inert in the acid electrolytes[16] and its surface favors the reductive deposition of Pt.[17–19] By depositing very small Pt particles or clusters onto Au nanoparticles of about 10 nm and by loading the Pt^Au particles onto a conventional carbon support, we have discovered a synthetic approach that prevents finely dispersed Pt particles from being pocketed in the micropores of the supporting carbon materials. By adjusting the Pt loading on the Au nanoparticles, we demonstrate that the exposed percentage of Pt atoms in such a model electrocatalyst can be enhanced to nearly 100%, that is, virtually every Pt atom in the electrode becomes available and catalytically active for the electrochemical reactions. This method makes the most efficient use of Pt in electrocatalysis and may also be exploited to improve the utilization of precious metals in other catalysts.

The deposition of Pt onto Au nanoparticles was carried out by reducing $K_2[PtCl_6]$ with hydrogen in a solution that contained Au particles with a narrow size distribution (10.0 ± 1.2 nm) and polyvinylpyrrolidone (PVP). The prepared samples were coded as Pt_m^Au, in which m denotes the atomic Pt/Au ratio within the nanoparticles. Figure 1 shows the UV/Vis and X-ray photoelectron spectroscopy (XPS) spectra of Au particles with varying amounts of deposited Pt. In the UV/Vis spectra (Figure 1 A), the deposition of Pt onto the Au surface is characterized by a continued weakening of the gold plasmon absorption at around 520 nm.[17,20] At about $m = 2.0$, the plasmon absorption becomes almost invisible. In the XPS spectra (Figure 1 B), continued weakening of the $Au^0$4f signals at 83.9 and 87.8 eV[21,22] is accompanied by the appearance and strengthening of the $Pt^0$4f signals at 70.8 and 74.3 eV with increasing Pt content. These results suggest that the surface of the Au nanoparticles becomes completely covered with Pt overlayers that shield the underlying Au surface from the XPS detection when the number of deposited Pt atoms reaches twice the number of Au atoms of the supporting Au nanoparticles (that is, $m = 2.0$).

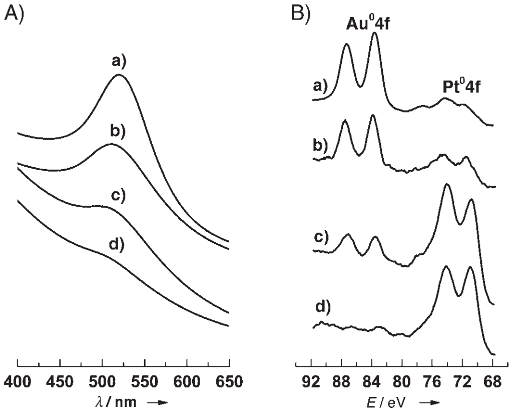

Figure 1. UV/Vis (A) and XPS (B) spectra of: a) $Pt_{0.05}$^Au; b) $Pt_{0.2}$^Au; c) $Pt_{1.0}$^Au; d) $Pt_{2.0}$^Au.

Using the atomic Pt/Au ratios measured by XPS, we estimated the number density of Pt atoms (N_{Pt}: number of Pt atoms per nm^2 of Au surface) at the Au surface by considering the initial Au particles as spheres and by assuming that the

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area for a single Au atom is 7.87×10^{-2} nm^2.[23–25] For example, the N_{Pt} values are 3, 12, and 62, respectively, for $Pt_{0.05}$^Au, $Pt_{0.2}$^Au, and $Pt_{1.0}$^Au particles (see the Supporting Information). As the size of a Pt atom is basically the same as that of an Au atom, the atomic density of the metallic platinum surface is 1.3×10^{15} per cm^2 (that is, 13 Pt atoms per nm^2),[26] so the data clearly indicate that the deposited Pt atoms in the samples with $m \leq 0.2$ are highly dispersed. In particular, the deposited Pt atoms at $m = 0.2$ may form a complete monoatomic layer (about 12 Pt atoms per nm^2 of Au surface) that covers the Au particles. When m is sufficiently small, for example $m \leq 0.05$, the density of the deposited Pt atoms is less than 3 Pt atoms per nm^2 of the Au surface, which suggests that the deposited Pt would exist as very small cluster islands or two-dimensional rafts.

Figure 2 shows transmission electron microscopy (TEM) images of the as-prepared and carbon-supported Pt_m^Au particles, which assume an approximately spherical shape. Although the size of Pt_m^Au particles generally tends to increase with an increase in m, the sizes of $Pt_{0.05}$^Au (Figure 2b) and $Pt_{0.03}$^Au (not shown) particles are apparently very close to that of the original Au particles (Figure 2a). According to Henglein,[17] the size of the spheric Pt_m^Au particles ($d_{Pt_m\wedge Au}$) can be estimated by using Equation (1) in which n_{Pt}/n_{Au} is the number ratio of Pt and Au atoms in the particles ($n_{Pt}/n_{Au} = m$); V_{Pt}/V_{Au} is the volume ratio of Pt and Au atoms, which is 0.89;[25] d_{Au} in our case is 10 nm; and the calculated $d_{Pt_m\wedge Au}$ sizes are 14.1, 12.4, 11.3, and 10.7 nm at $m = 2.0$, 1.0, 0.5, and 0.2, respectively. These sizes agree well with the TEM sizes of the Pt_m^Au particles (see Figure 2 and the Supporting Information). In particular, the particle size of $Pt_{0.2}$^Au (that is, $d_{Pt_m\wedge Au} = 10.7$ nm) suggests a thickness for the deposited Pt layer in this sample of 0.35 nm. This value also agrees well with the calculation based on the atomic Pt/Au ratio measured with XPS when the Au particles are completely covered with a monoatomic layer of Pt, as the thickness is equivalent to the diameter of a Pt atom (0.36 nm).[25]

$$d_{Pt_m\wedge Au} = [(n_{Pt}/n_{Au})\,(V_{Pt}/V_{Au}) + 1]^{1/3}\, d_{Au} \qquad (1)$$

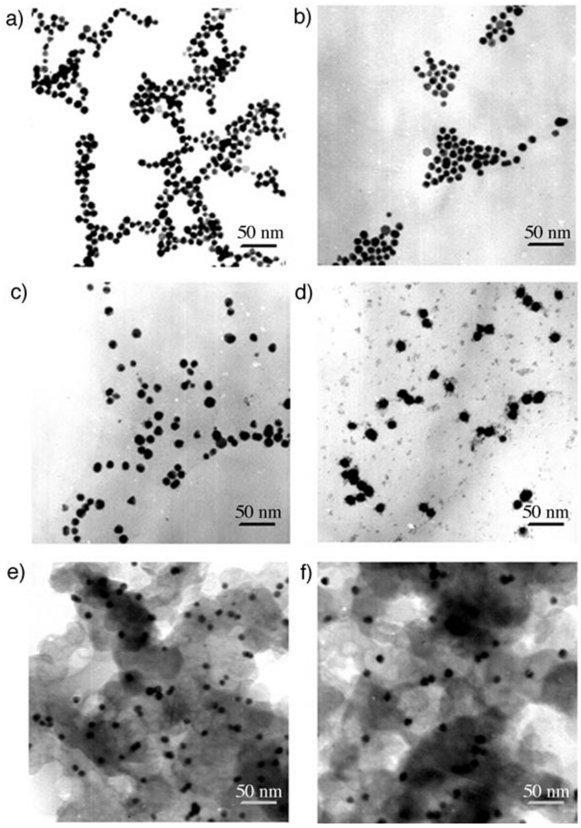

Figure 2. TEM images of: a) Au; b) $Pt_{0.05}$^Au; c) $Pt_{0.2}$^Au; d) $Pt_{1.0}$^Au; e) $Pt_{0.05}$^Au/C; f) $Pt_{1.0}$^Au/C.

In reference to the sample of $m = 0.2$, the deposited Pt in samples of $m = 0.1$, 0.05, and 0.03 would correspond up to 1/2, 1/4, and 1/6 monoatomic Pt layers, respectively, and thus would be insufficient to fully cover the Au surface. The indistinguishable particle sizes between Au and $Pt_{0.05}$^Au samples in the TEM images (Figure 2a and b) also support that the deposited Pt exists as very small cluster islands or 2D Pt rafts.

To study the potential of Pt_m^Au nanoparticles in the enhancement of Pt utilization in Pt-based electrocatalysts, the as-prepared Pt_m^Au particles were supported with the Vulcan XC-72 carbon blacks to make Pt_m^Au/C catalysts for electrochemical characterization. TEM images of the Pt_m^Au/C samples (Figure 2e and f) show that the Pt_m^Au particles in the catalysts are isolated from each other and maintain their original high dispersion.

An important parameter for Pt-based electrocatalysts is the electrochemically active surface (EAS, m^2 per g Pt) of Pt in the electrode catalyst. As in most electrochemical studies,[27,28] we measured the EAS of Pt_m^Au/C catalysts by using the hydrogen-desorption or hydrogen-electrooxidation peaks on the cyclic voltammetry (CV) curves in acidic media (0.5 M H_2SO_4; see the Supporting Information). Any hydrogen electrooxidation peak in the CV curves should arise from the presence of Pt in the Pt_m^Au/C electrocatalyst as carbon-supported gold nanoparticles (Au/C) without Pt are inactive for the adsorption and electrooxidation of hydrogen.[16] Thus, the EAS of Pt_m^Au/C catalysts can be obtained according to Equation (2),[29] in which Q_H is the charge consumed for the

$$\mathrm{EAS} = (Q_H/Q_e)\,A_{Pt}/W_{Pt} = (A_{Pt}/Q_e)\,Q_H/W_{Pt} \qquad (2)$$

electrooxidation of adsorbed hydrogen on the Pt surface (i.e., the electrode catalyst), which is equivalent to the calibrated area of the hydrogen-electrooxidation peak; Q_e is the elementary charge or charge of an electron ($Q_e = 1.602\times10^{-19}$ C); A_{Pt} is the averaged atomic area of surface Pt atoms, which is 7.69×10^{-2} nm^2 according to the atomic density of a Pt surface which is 1.3×10^{19} per m^2;[26] and W_{Pt} is the Pt loading at the working electrode. This equation is based on the well-established hydrogen-adsorption stoichiometry at a Pt surface (H:Pt = 1:1).[4,30]

Therefore, the data of CV measurements allow us to count the number of exposed Pt atoms (N_s) as the number of adsorbed H atoms (N_H) on the electrode catalyst, that is, $N_s = N_H = Q_H/Q_e$. Thus, the ratio of N_s or N_H to the total number of

Pt atoms (N_t) in the electrode catalyst gives the utilization percentage of Pt [Eq. (3)].

$$U_{pt} = N_s/N_t = N_H/N_t \tag{3}$$

Listed in Table 1 are the Pt utilization data from the CV measurements. It is apparent that the EAS and U_{Pt} data for the Pt$_m$^Au/C samples are close to those of a Pt/C catalyst at $m \geq 0.5$. Prominent enhancement in EAS and U_{Pt} emerges when m becomes lower than 0.2. In particular, when m is further decreased to 0.05 or less, the EAS and U_{Pt} increase to approach 234 m^2 per g Pt and 100 %, respectively, which are at least twice those of the Pt-based electrocatalysts documented in most reports.[28,31]

The Pt$_m$^Au/C catalysts were used for the electrooxidation of methanol. Figure 3 shows half curves of the normalized cyclic voltammetry of this electrooxidation. It is evident that the normalized current increases remarkably with decreasing value of m, and that the current varies little from the normal Pt/C electrode when $m \geq 0.5$. The current variation over the Pt$_m$^Au/C catalysts mimics the change of U_{Pt} in these catalysts. The last column of Table 1 shows the quantitative mass activity of Pt in the Pt$_m$^Au/C catalysts, which is defined as the current of methanol electrooxidation over a milligram of Pt in the electrode. The mass–activity data follow the same trend as the EAS and U_{Pt} results, thus proving that the electrocatalytic activity of Pt is directly associated with the utilization or dispersion of Pt in the electrode catalyst. It is not surprising that Pt in Pt$_{0.03}$^Au/C and Pt$_{0.05}$^Au/C catalysts exhibit virtually the same mass activity for the electrooxidation of methanol as the Pt utilization in these two catalysts already approaches 100 %.

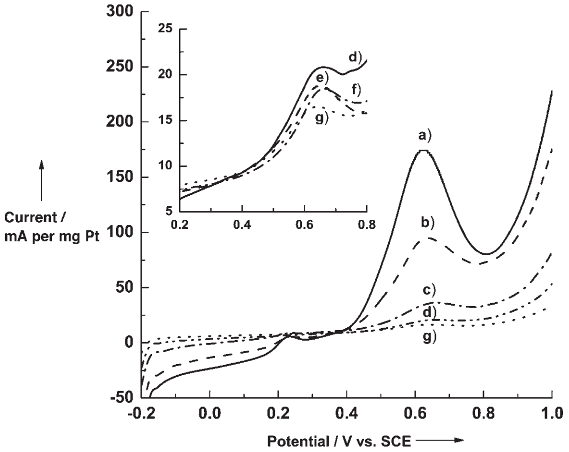

Figure 3. Cyclic voltammetric curves for the electrooxidation of methanol (scan rate: 20 mV s^{-1}, 0.5 M H_2SO_4, 2 M CH_3OH, 298 K) with the following electrocatalysts: a) Pt$_{0.05}$^Au/C; b) Pt$_{0.1}$^Au/C; c) Pt$_{0.2}$^Au/C; d) Pt$_{0.5}$^Au/C; e) Pt$_{1.0}$^Au/C; f) Pt$_{2.0}$^Au/C; g) Pt/C.

To understand the electrocatalytic stability of the Pt$_m$^Au/C catalysts, the Pt$_{0.05}$^Au/C electrode catalyst was subjected to long-term repeated scanning by cyclic voltammety in 0.5 M H_2SO_4 with 2 M CH_3OH at 298 K, as described previously by Lebedeva and Janssen.[32] The change in peak current density (0.65 V vs. SCE) of the electrooxidation of methanol is shown in Figure 4 for 240 cycles. The working period of the electrocatalyst in this specific type of measurement is proportional to the number of scan cycles; each scan cycle lasted for 2 min, and the total working period was about 8 h. The data in Figure 4 show stable electrocatalytic activity of the catalyst electrode; variation in the current density was less than 5 %. Therefore, the finely dispersed Pt cluster islands prepared for this study are suitable electrode catalysts for the electrooxidation of methanol.

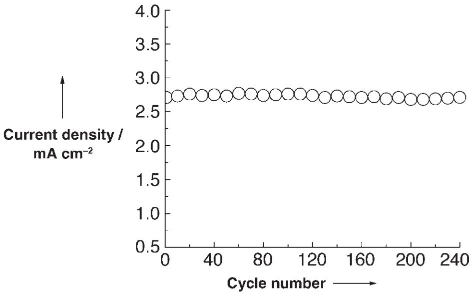

Figure 4. Stability of the Pt$_{0.05}$^Au/C electrocatalyst over 240 cycles of methanol electrooxidation.

It is not known at present whether the Pt in Pt$_m$^Au/C exists as 3D clusters of about 1 nm or smaller in diameter or as 2D atomic rafts at the gold surface. Although small particles of transition metals have a long history in heterogeneous catalysis, supported metal particles with sizes smaller than 1 nm have rarely been investigated even in the field of heterogeneous catalysis. A few reports show that metal clusters of smaller than 1 nm would have significantly differ-

Table 1: Loading, surface concentration, and utilization of Pt and the electrochemical properties of the Pt electrocatalysts.

Catalyst	[Pt] [mg cm^{-2}]	N_t [$\times 10^{17}$ cm^{-2}]	Q_H [mC cm^{-2}]	N_s [$\times 10^{16}$ cm^{-2}]	EAS [m^2 g^{-1}]	U_{Pt} [%]	Catalytic activity[a] [mA mg^{-1}]
Pt/C	0.22	6.79	11.2	7.00	24.2	10.3	7.3
Pt$_{2.0}$^Au/C	0.29	8.95	12.9	8.06	21.2	9.0	9.5
Pt$_{1.0}$^Au/C	0.19	5.86	10.6	6.63	26.6	11.3	8.5
Pt$_{0.5}$^Au/C	0.11	3.39	6.5	4.06	28.1	12.0	11.6
Pt$_{0.2}$^Au/C	0.05	1.54	6.1	3.81	58.1	24.7	26.2
Pt$_{0.1}$^Au/C	0.03	0.93	8.2	5.13	130.2	55.4	83.1
Pt$_{0.05}$^Au/C	0.02	0.62	9.9	6.15	233.3	99.2	162.5
Pt$_{0.03}$^Au/C	0.012	0.37	5.9	3.68	234.1	99.5	161.6

[a] For methanol oxidation, at 0.65 V.

ent chemical properties than larger metallic particles as a result of their strong interaction with the supporting material.[13–15] Nevertheless, very small Pt entities (≤ 1.0 nm) supported on Au nanoparticles are still very effective for the electrooxidation of methanol. This activity may be related to the inert nature of the supporting gold surface. Surface-enhanced Raman spectroscopic studies of chemisorptions on ultrathin Pt-group metal films of 2–3 monolayer thickness deposited on Au substrates show that surface chemical properties of the Pt-group metals were not significantly affected by the presence of an underlying Au substrate.[33,34] It is also interesting that the very small noble-metal clusters on the Au particles did not react with each other, which may have important implications in understanding the role of the metal in conventional chemical catalysis of particles smaller than 1–2 nm in diameter.

In conclusion, we have demonstrated an approach to enable the most efficient use of Pt in electrocatalysts and to allow every Pt atom to assume the function of a catalytic site for an electrochemical reaction. The approach makes use of Au nanoparticles of about 10 nm in diameter as an immediate support for very small Pt entities with 100% dispersion. Although the highest dispersion of Pt is realized only with low Pt loadings ($m \leq 0.05$), loadings could be significantly increased by decreasing the size of the supporting Au particles (e.g., 2–5 nm). The effect of changing the size of the Au particles is being investigated and progress will be reported in the near future.

Experimental Section

The deposition of Pt onto Au nanoparticles was carried out by reducing $K_2[PtCl_6]$ with hydrogen in a solution containing Au particles (ca. 10.0 nm in diameter) and PVP. Au nanoparticles were prepared according to the methods of Enustun and Turkevich.[35] The gold concentration was kept constant at 1.25×10^{-4} mol L^{-1} for each preparation, whereas the amount of $K_2[PtCl_6]$ in the solution was varied to change the overall atomic Pt/Au ratios from 0.02 to 2.0. For comparison, Pt-only nanoparticles were also prepared under the same conditions in the absence of Au nanoparticles, as described in our earlier work.[36]

Colloids (Au, Pt, Pt_m^Au) were supported on high-surface-area Vulcan XC-72 carbon (ca. 250 m^{2}g^{-1}) by combining a dispersion of the colloids with a suspension of the carbon support in ethanol. The mixture was vigorously stirred for 48 h after sonication (30 min). The powdered product was isolated by filtration, washed extensively with deionized water, and dried at 110°C for 2 h. Inductively coupled plasma–atomic emission spectroscopy (ICP–AES) showed that the atomic Pt/Au ratios in the final catalysts agreed well with those in the preparation mixtures, thus indicating that Pt deposition from the mixture was complete.

Cyclic voltammetry was performed in 0.5 M H_2SO_4 with a thermostated three-electrode glass cell at room temperature. The working electrode was prepared by using ultrasound to disperse the catalyst powders in 5% Nafion solution (Aldrich). The resulting dispersion was spread over PTFE-treated carbon paper (DuPont) and then dried in air. The catalyst loading at the working electrode was 4 mg cm^{-2}. A saturated calomel electrode was used as the reference electrode and a Pt foil of 1×1 cm^2 was used as the counter electrode.

Before CV measurements were recorded, the electrolyte was purged with nitrogen (99.9%) for 30 min, and several tens of CV cycles (sweeping rate: 50 mV s^{-1}) were performed between –0.24 and 1.0 V to stabilize the electrode surface. Methanol was electrooxidized in an electrolyte containing 0.5 M H_2SO_4 and 2 M CH_3OH in a potential range from –0.20 to 1.0 V at a sweeping rate of 20 mV s^{-1}.

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charge and surface area are C and m^2, respectively. The value becomes 0.21 when μC and cm^2 are used.

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