Enhanced Electrochemical Performances of Nanoporous Gold by Surface Modification of Titanium Dioxide Nanoparticles

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We reported novel nanoporous gold (NPG) with surface modified by TiO$_2$ nanoparticles. The as-fabricated sample showed larger effective area than bare NPG. Microstructure characterization demonstrated that the TiO$_2$ nanoparticles effectively suppressed the coarsening of the nanoporous structure by the reaction with gold ligaments. The resultant porous nanocomposite with rough ligament surfaces was proofed to spontaneously possess enhanced catalytic performance towards methanol oxidation. This result would yield an effective and inexpensive method to improve NPG’s catalytic activity. [doi:10.2320/matertrans.MAW201014]

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1. Introduction

Recently, nanoporous gold (NPG) has been the focus of numerous scientific studies because of its unique, three-dimensional nanostructure$^{1,2}$ and its interesting catalytic, electronic, and optical properties.$^{3-8}$ Gold nanoparticles have been researched extensively since it was discovered that they can catalyze many useful chemical reactions, but NPG has preferable features, especially for use as catalytic electrodes in electrochemical devices.$^{9,10}$ For example, unlike gold nanoparticle electrodes, free-standing NPG electrodes do not require metal oxide support, so they are more easily incorporated into the devices. This feature provides significant benefits in both the manufacturing and recycling processes.

To date, several successful efforts to enhance the catalytic activity of NPG have been reported; however, these techniques depend largely on adding platinum and palladium,$^{9-12}$ which are more than or comparably expensive to gold. Considering the expected extensive proliferation of devices that will utilize this technology, such as fuel cells, the use of precious metals must be minimized. In order to accomplish this goal, a desirable strategy is to employ a method that has been applied in research related to gold nanoparticles, i.e., making composites with metal oxide.

Over the years, there has been much discussion about the role of metal oxide in gold nanoparticle-metal oxide systems. Many different metal oxides have been tested for use in the composite materials, and it has been found the extent to which chemical reactions can be catalyzed by the composite depends on the type of metal oxide on which the gold nanoparticles are embedded.$^{13}$ However, only a few studies of composites made with metal oxides and NPG have been conducted to determine their potential for advantageous use in the prospective applications.$^{14}$

In this work, we modified the surface of NPG by adding metal oxide nanoparticles and investigated the structure, surface area, and catalytic activity of these materials for the oxidation of methanol. We chose titanium dioxide because this approach had shown some promise in recent research.$^{13,15-18}$ Contrary to the assumption that embedding catalytically inert substances would decrease the effective surface area of the NPG, it was found that the effective surface area actually increased after appropriate annealing, so that the TiO$_2$-NPG combination provides a better catalytic effect than NPG alone.

2. Experimental Section

2.1 Materials

All chemicals were commercially obtained and used as received. Ultrapure water (resistivity $> 18$ MΩ cm) was used throughout the experiments. Glassy carbon plates for electrochemical experiments were obtained from BAS Inc. Water-dispersed TiO$_2$ (MPT-427, rutile phase, particle size of 50–100 nm, obtained from Ishihara Sangyou Kaisha, Ltd.) was used to modify the surface of the NPG. Au$_{35}$Ag$_{65}$ white gold leaf, from which the parent material for NPG was prepared, was commercially obtained.

2.2 Sample fabrications

NPG was prepared by dealloying, the process to elute only silver in HNO$_3$ (69%) at room temperature for 30 min. After washing with ultrapure water, the NPG leaves were placed on a glassy carbon plate. The water-dispersed TiO$_2$ was distilled 15 times by ethanol and immediately dropped on the NPG, giving a TiO$_2$ loading of about 60 μg/cm$^2$. Then, the NPG leaf with TiO$_2$ and two other bare NPG leaves on carbon plates were kept in a desiccator for an hour at a pressure of 0.1 atm in order to eliminate residual water and ethanol. Leaving one bare NPG leaf, the other two samples were annealed at 373 K for an hour in air. Three different samples, i.e., TiO$_2$-NPG; bare, annealed NPG; and bare, non-annealed NPG were finally fabricated. All of the samples were trimmed to measure $5 \times 5$ mm, with an area of 25 mm$^2$.

2.3 Electrochemical experiments and characterizations

Electrochemical catalytic activity was determined in a 1.0 M CH$_3$OH + 0.5 M KOH aqueous solution. A Pt plate and an AgCl electrode were employed as the counter electrode and the reference electrode, respectively. The effective area of each sample was measured with the same apparatus as for catalytic activity, but in 0.5 M H$_2$SO$_4$. The prepared samples were characterized by scanning electron
microscope (SEM, JEOL JIB-4600F) and transmission electron microscope (TEM, JEM-2100F, 200 kV).

3. Results

3.1 SEM investigation

SEM images of the fabricated samples are shown in Fig. 1. The average pore sizes of bare-non-annealed and bare-annealed NPG were about 60 and 80 nm, respectively, because the nanostructure coarsened. Coarsening at high temperatures is one of the distinct effects on NPG structure that decreases the effective surface area and thereby impairs catalytic performance. When the three pictures in Fig. 1 are compared, however, it is found that the pore size of TiO$_2$-NPG remained the same, even after annealing. It is assumed that the TiO$_2$ embedded on the surface of the NPG inhibited the diffusion because diffusion of atoms at the surface, which plays an important role in morphology determination, is disturbed at the interface between TiO$_2$ and gold. Though not completely homogeneously dispersed, the nanoparticles did not aggregate to make a huge cluster up to the order of micrometer.

3.2 Electrochemical experiments

In order to measure the effective surface area, current-voltage (CV) curves were measured in 0.5 M sulfuric acid. The anodic peak in Fig. 2 corresponds to gold reduction reaction. Therefore, the surface area is approximately calculated by dividing the integrated intensity of this peak by the scanning rate (0.1 V/s) and the amount of the charge needed to reduce the specific area of a gold monolayer (386 µC/cm$^2$). Intuitively, TiO$_2$-NPG is expected to possess the smallest effective area since it was annealed and had its effective surface covered by TiO$_2$ that is inert to methanol oxidation. Contrary to the assumption, however, the CV curves showed that TiO$_2$-NPG possessed the largest effective area among the three samples (Table 1), which is about 1.2 times larger than that of bare-non-annealed NPG. As it was proven in the previous work that the 3D volume

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Fig. 1 SEM pictures of samples. (a) Bare-non-annealed (b) Bare-annealed (c) TiO$_2$-annealed

Fig. 2 CV-curves for effective area measurements.
ratio between gold ligaments and nanopore channels were almost 50:50. The effective area per mass in the Table 1 (referred as A) were calculated as 

\[
A = \frac{2S}{d \cdot V}
\]

where S, d, V refers to the surface area (m\(^2\)), the density of gold (0.0193 g/mm\(^3\)), and the volume of NPG (5 mm \(\times\) 5 mm \(\times\) 100 nm), respectively.

Catalytic activity toward methanol oxidation was evaluated in alkaline methanol solution (Fig. 3). The cathodic peak at around 0.27 V and the anodic peak at around -0.03 V correspond to methanol oxidation and gold reduction, respectively. The catalytic activity is basically measured by the current. The three CV curves in Fig. 3 are consistent with the results of surface area measurement, i.e., TiO\(_2\)-NPG with the highest performance; bare-non-annealed sample in the middle; and the bare-annealed sample with the lowest performance. A slight shift toward low potential was observed in the two peaks, which indicates that the gold surface of TiO\(_2\)-NPG is chemically more active than the surfaces of the other two samples (Table 2).

The TiO\(_2\) employed was actually photocatalytically active under visible light by surface modification with platinum oxide (PtO, the reason we used this TiO\(_2\) is mentioned later). Still, its content is quite low, and indeed, no peaks corresponding to platinum-related reactions were observed in the CV curves obtained from TiO\(_2\) alone in alkaline methanol solution, so the catalytic effect from incorporated platinum can be negligible in this work.

### 3.3 TEM investigation

TEM picture and FFT patterns of the composite sample are shown in Fig. 4. It was found that the TiO\(_2\) nanoparticle was partially covered by gold, indicating reaction between gold and TiO\(_2\) took place during annealing. Between gold atoms and TiO\(_2\), very good contact between the metal and the oxide can be observed around the square c, whereas an interface layer such as amorphous films has not been seen. The FFT patterns a\(-d\) were obtained from squares a\(-d\), respectively. The FFT pattern of gold matrix obtained from the square a is that of fcc structure with incident [001]. At the square b closer to the coherent interface, the FFT pattern of gold changed as in the pattern b: two spots weakened (pointed out by white arrows), two spots stemming from TiO\(_2\) pattern.

### Table 1 Effective areas for prepared samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Effective area (mm(^2))</th>
<th>Effective area per mass (m(^2)/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO(_2)-annealed</td>
<td>169</td>
<td>7.00</td>
</tr>
<tr>
<td>Bare-non-annealed</td>
<td>143</td>
<td>5.92</td>
</tr>
<tr>
<td>Bare-annealed</td>
<td>113</td>
<td>4.67</td>
</tr>
</tbody>
</table>

### Table 2 Peak potentials for prepared samples in Fig. 3.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Methanol Oxidation (V)</th>
<th>Au Reduction (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO(_2)-annealed</td>
<td>0.267</td>
<td>-0.023</td>
</tr>
<tr>
<td>Bare-non-annealed</td>
<td>0.275</td>
<td>-0.025</td>
</tr>
<tr>
<td>Bare-annealed</td>
<td>0.275</td>
<td>-0.026</td>
</tr>
</tbody>
</table>
(circle), and another two spots unique to the gold around the interface (square). At the square on the interface, the FFT pattern becomes the combination of the pattern b and the pattern d solely from TiO₂. The gold ligaments surrounding TiO₂ nanoparticles also have a high curvature because of the reaction (as seen in the white circle in TEM picture), resulting in the TiO₂-NPG composite generally has a much rough surface in comparison with the bare NPG.

4. Discussion and Conclusion

Our initial aim of this study was to synergistically enhance the catalytic activity of NPG by combining it with the photocatalytic activity of the employed TiO₂ under visible light. However, contrary to previous reports, almost no significant change was seen between the CV curves taken under visible light (12000 lx, fluorescent lamp).

The improved catalytic activity of TiO₂-NPG is attributed to the Au-TiO₂ interface in two aspects. First, although the effective area initially decreased when the TiO₂ nanoparticles were embedded, the gold atoms diffused and climbed up the particles during the annealing process schemed in Fig. 5. As a result, the effective area was recovered and even increased, resulting in improved catalytic activity. It needs to be elucidated if coarsening of nanostructure was prohibited even inside the NPG, where the effective contact between TiO₂ and gold atoms is not as often as that at the geometrical surface of the sample. Still, considering that the geometrical surface area corresponded to about a sixth of effective surface area, it is not illogical that the diffusion restriction only at the interface possibly affected even the entire morphology during annealing. Second, the diffused gold layers on TiO₂ have a greater curvature than that of the bare NPG surface. Since the sharply curved surface contains a large number of surface terraces and local high-indexed crystal facets, these areas become more activated to the methanol oxidation and may be responsible for the peak shift towards lower potential. Moreover, the contact between gold and TiO₂ may lead to the charge transfer between the metal and oxide, resulting in the enhanced electrochemical performance.

In summary, a TiO₂-NPG composite was fabricated, and it was shown to have improved catalytic activity toward methanol oxidation than the bare NPG. The improvement is attributed to the Au-TiO₂ interface, and it eliminates the need for the future use of rare metals. Furthermore, there is significant potential for improving the catalytic activity of NPG by combining it with other metal oxides, such as zinc oxide and cerium oxide. We hope this work will stimulate additional research of economical and environmentally viable methods for producing effective catalytic electrodes for direct-methanol fuel cells and other electrochemical devices.

Acknowledgments

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REFERENCES