Immobilization of Au Nano Particles Using the Durable Hydrophilic Polymer Surface Fabricated by Plasma-Assisted Method

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1. Introduction

We have reported a novel method to introduce a durable surface wettability and minimize its decay with time on several hydrophobic polymers, such as polyethylenenaphthalate, polyethylene, and nylon-12.[1-4] Figure 1 shows the schematic illustration for the fabrication of durable hydrophilic surface. This method involves sorption of methylvinylether-maleic anhydride copolymer (VEMA) into the surface layer and immobilization by a plasma-assisted cross-link reaction. Hydrolysis of VEMA follows to generate carboxyl groups on the surface. The durable hydrophilic surface thus introduced has been confirmed by not only the measurement of water contact angle but also demonstration of long term stability of surface lubricity on the urethane-made catheter. The durable hydrophilic surface can make several bio-application works. For example, model oligo-DNA was immobilized onto the durable hydrophilic film (LDPE-VEMAC film) for the development of DNA chips.[5] We have also reported the development of a novel fabrication of self-assembled phospholipid layer by the use of LDPE-VEMAC film and its bio-application as a bio-sensor and bio-reactor immobilizing the bio-molecules such as enzyme and antibody on the self-assembled phospholipid layer.[6-10]

![Schematic illustration for the fabrication of durable hydrophilic surface.](image-url)
The development and implementation of reusable catalysts in organic chemistry is becoming more important with increasing environment awareness and the current focus on green chemistry initiatives. Small-crystal-size gold (Au nanoparticles) supported on inorganic oxides or active carbon has recently attracted considerable attention, since these catalysts are able to promote the selective oxidation of alcohols.\[11-13\] It was also known that the support could affect on the activity of the immobilized Au nanoparticles.\[12, 13\] Polymer gel and particle were also used as a support.\[11\] In this paper, we synthesized the polymer film immobilizing Au nanoparticles by the use of a durable hydrophilic surface fabricated by the plasma-assisted method. 2-Aminoethanethiol (AET) was introduced on the LDPE-VEMAC film, and then Au nanoparticles were immobilized on the film by the reaction of thiol group and Au. To increase the content of immobilized Au nanoparticles, VEMAC was introduced on the LDPE-VEMAC film with hexamethylenediamine (HMDA) as a spacer. Preliminarily the activity of this film was evaluated with the oxidation of bezyl alcohol in a basic aqueous solution.

2. Experimental
2.1 Immobilization of 2-aminoethanethiol and hexamethylenediamine on the LDPE-VEMAC film
The LDPE-VEMAC film was prepared according to the method reported previously.\[6\] The LDPE-VEMAC film was soaked in a mixture of water (5 ml) and 0.25 mol/l 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDC) solution (1 ml) at 30 °C for 2 h. After adding 0.25 mol/l 2-aminoethanethiol (AET) or hexamethylenediamine (HMDA) solution (1 ml), the film was kept at 30 °C for 20 h. After then the film was washed with water and dried in vacuo.

2.2 Immobilization of VEMAC onto the LDPE-VEMAC film immobilizing HMDA
VEMA (100 mg) was dissolved into dry THF (40 ml). The LDPE-VEMAC film immobilizing HMDA (1 cm X 3 cm) was soaked into a VEMA solution (20 ml) and kept at 37 °C for 12 h. The film was washed with THF and dried in vacuo. This film was immersed into 0.1 mol/l NaOH aqueous solution (200 ml) for 10 min, and then 1 mol/l HCl solution (100 ml) for 10 min. The film was thoroughly washed with water and dried in vacuo to obtain the film introducing VEMAC, LDPE-HMDA-VEMAC film.

2.3 Introduction of AET onto the LDPE-HMDA-VEMAC film
The LDPE-HMDA-VEMAC film was soaked into 0.25 mol/l EDC solution (5 ml) at 30 °C for 2 h. To this solution was added 0.25 mol/l AET solution (5 ml). This reaction mixture was kept at 30 °C for 12 h. The film was washed with water and dried in vacuo to obtain the film introduced AET, LDPE-HMDA-VEMAC-AET film.

2.4 Immobilization of Au nanoparticles
The Au nanoparticle solution (Gold colloid (5 nm), EMGC5, 5X10\(^{13}\) number of particles/ml, Funakoshi Co.) was diluted with water by 10 times. Three films of LDPE-VEMAC film introduced AET (LDPE-AET film) or LDPE-HMDA-VEMAC-AET film were soaked into 5 ml of the diluted Au nanoparticle solution. The films were kept at room temperature. Progressive changes in absorbance at 515 nm were observed to estimate the amount of immobilized Au nanoparticles.

2.5 Procedure for benzyl alcohol oxidation \[11\]
A test tube was placed with bezyl alcohol (27.0 mg, 0.25 mmol), \(\text{K}_2\text{CO}_3\) (103.7 mg, 0.75 mmol), \(\text{H}_2\text{O}\) (5 ml), and film immobilizing Au nanoparticles (1 cm X 1 cm). Free zone capillary electrophoresis was carried out at 260 nm. Electrophoresis of the reaction mixture was performed using the capillary in 25 mM sodium borate solution. Sample solution was introduced into the capillary at the anodic side and was charged with 12 kV constant voltage.

3. Results and Discussion
3.1 Immobilization of Au nanoparticles
Figure 2 shows the schematic representation of the immobilization of Au nanoparticles onto the LDPE-AET and LDPE-HMDA-VEMAC-AET
film. Method A is that the Au nano particles are immobilized on LDPE-AET which is the film introduced 2-aminoethanthiol (AET) to the LDPE-VEMAC. This film was termed LDPE-AET-AU film. Method B is applied to increase the amount of Au nano particles immobilized. Thus, VEMAC was immobilized on LDPE-HMDA on which hexamethyl diamine was introduced on LDPE-VEMAC film, and then AET was reacted with VEMAC (LDPE-HMDA-VEMAC-AET film). Au nano particles were immobilized on LDPE-HMDA-VEMAC-AET film to obtain LDPE-VEMAC-Au film.

Table 1 shows the amount of Au nano particles on LDPE-AET-Au and LDPE-VEMAC-Au films. The amount of Au nano particles on LDPE-VEMAC-Au film was about 8.5 times larger than that on LDPE-AET-Au film.

Table 1  Amount of Au Nano Particles per Area

<table>
<thead>
<tr>
<th>Film</th>
<th>Number of particles / cm²</th>
</tr>
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<tbody>
<tr>
<td>LDPE-AET-Au</td>
<td>$4.76 \times 10^{11}$</td>
</tr>
<tr>
<td>LDPE-VEMAC-Au</td>
<td>$4.01 \times 10^{12}$</td>
</tr>
</tbody>
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3.2 Oxidation of benzyl alcohol with LDPE-AET-Au and LDPE-VEMAC-Au film

To confirm the activity of immobilized Au nano particles, the oxidation of benzyl alcohol with immobilized Au nano particles was carried out in basic aqueous solution. The result is shown in Table 2. Although the oxidation of benzyl alcohol did not proceed with LDPE-AET-Au film for 24 h within a detectable extent, the reaction with LDPE-VEMAC-Au film gave benzoic acid in 15 % yield.

We also carried out the oxidation of dimethyl phenyl silane with these films (Scheme 1). But this reaction with these films did not proceed within a detectable extent in this experimental condition.

Table 2  Oxidation of Benzyl Alcohol with Immobilized Au Nano Particles

<table>
<thead>
<tr>
<th>Film</th>
<th>Time (h)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LDPE-AET-Au</td>
<td>24</td>
<td>0</td>
</tr>
<tr>
<td>LDPE-VEMAC-Au</td>
<td>24</td>
<td>15</td>
</tr>
</tbody>
</table>

Scheme 1  Oxidation of dimethyl phenyl silane with immobilized Au nano particles.

4. Conclusion

The conclusions drawn from the present study can be summarized as follows.

We synthesized the polymer film immobilizing Au nano particles by the use of a durable hydrophilic surface fabricated by the plasma-assisted method. Two kinds of methods were used to immobilize Au nano particles. The LDPE-VEMAC-AU film (method B) could immobilize larger amount of Au nano particles than LDPE-AET-Au film. It was also shown
that the oxidation of benzyl alcohol proceeded in basic aqueous solution with LDPE-VEMAC-AU film.

We are now actively elaborating the optimization of preparation conditions to increase the amount of immobilized Au nano particles and the application to other reactions with the film prepared with this method.

References