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Catalytic decoloration of methyl orange solution by nanoporous metals

Masataka Hakamada, a Fumi Hirashima a and Mamoru Mabuchi a

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Nanoporous Au exhibit catalytic degradation of methyl orange (MO) solution while counterpart bulk Au does not. Other nanoporous metals such as Pd and Ni also exhibited the catalytic MO degradation. Because the degradation occurred under dark conditions, it is clearly distinguished from photocatalytic degradation conventionally observed in TiO 2 and ZnO.

The toxic pollution caused by azo dyes in the environment has attracted much attention recently. Various catalysts and photocatalysts have been investigated to remove such environment pollutants. 1–4 Nanosized materials such as nanoparticles, nanotubes and their composites are promising due to their larger surface-to-volume ratios and subsequent increase of reaction rate in catalysis 5 and photocatalysis. 6 On the other hand, nanoporous metals with nanosized pores and ligaments are emerging nanostructured materials and can be readily fabricated by dealloying (selective dissolution of less noble metals from binary alloys). 7 The open-cell nanoporous structure of metals offers many interesting properties, such as catalytic 8–13 electrical, 14 and piezoelectric properties. 15,16 Nanoporous metals have surface atomic irregularities such as defects and strain, which cause these peculiar properties to be distinguished from other nanomaterials. 17,18

Several studies have reported that nanoporous Au exhibits catalysis during the oxidation of CO 8–12 and methanol, 13 while its counterpart, bulk Au without a porous structure, does not. In the present work, we show the catalytic degradation of a dye solution by nanoporous Au, which is distinguished from the conventional photocatalytic effect known in semiconductor oxides such as TiO 2 and ZnO.

Nanoporous Au was fabricated by dealloying a Au 0.3 Ag 0.7 sheet under various conditions of free and electrochemical corrosion. Detailed experimental methods are described in the Supporting Information. Figs. 1a–c are scanning electron micrographs of fabricated nanoporous Au. The average ligament size and pore diameter were larger in the sample fabricated by free corrosion at room temperature than in the two other nanoporous Au, as summarized in Table 1. Smaller pores and ligaments are well correlated to higher roughness factors (R) determined by cyclic voltammetry in 0.1 mol/L H 2 SO 4. 19 These trends are in agreement with the previous studies on nanoporous Au. 20,21 For comparison, pure Au, Au 0.7 Ag 0.3 and Au 0.3 Ag 0.7 rolled sheets was also prepared as bulk materials.

Methyl orange (MO), a typical azo used in the textile industry,
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ARTICLE TYPE

Table 1 Nanoporous Au and bulk Au samples subjected to decoloration of methyl orange (MO) solution.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Specification*</th>
<th>Au : Ag (atomic %)</th>
<th>Ligament diameter, (d_l) (nm)</th>
<th>Pore diameter, (d_p) (nm)</th>
<th>Roughness factor, (R)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Nanoporous Au (free corrosion at 263 K)</td>
<td>82 : 18</td>
<td>7.6</td>
<td>8.4</td>
<td>310</td>
</tr>
<tr>
<td>2</td>
<td>Nanoporous Au (free corrosion at 298 K)</td>
<td>92 : 08</td>
<td>21</td>
<td>18</td>
<td>270</td>
</tr>
<tr>
<td>3</td>
<td>Nanoporous Au (electrochemical dealloying)</td>
<td>81 : 19</td>
<td>5.4</td>
<td>5.2</td>
<td>430</td>
</tr>
<tr>
<td>4</td>
<td>Bulk Au</td>
<td>100 : 0</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>5</td>
<td>Bulk Au (\text{Au}<em>{10}/\text{Ag}</em>{90})</td>
<td>70 : 30</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>6</td>
<td>Bulk Au (\text{Au}<em>{8}/\text{Ag}</em>{92})</td>
<td>30 : 70</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

* Footnote text.

Sample 1. The initial concentration of MO was \(1.5 \times 10^{-4}\) mol/L in this experiment. After the immersion of Sample 1, the absorbance at the visible light wavelength range (400–700 nm) disappeared, which corresponds with the decoloration of the MO solution. However, the absorbance in an ultraviolet region of \(\lambda < 220\) nm increased after the immersion. The absorbance of the azo dye solution in the ultraviolet region is closely related to a short conjugated system of the organic molecule and typical of phenyl rings, while that in the visible light wavelength range is caused by azo group (–N=N–).\(^{23}\) MO contains two phenyl rings bridged by an azo group in its chemical structure; therefore it is surmised that MO decomposed to single phenyl ring compounds in the presence of nanoporous Au.

High-performance liquid chromatography (HPLC) studies using an instrument equipped with a UV-Vis photodiode array detector were also conducted using a reverse-phase setup. Fig. 4 shows the resulting chromatograms of the MO solution before and after the 1-week immersion of Sample 1. The initial MO solution showed single peaks for both wavelengths of \(\lambda = 210\) and 450 nm at the same retention times \((t_R)\) of 9.9 min, which suggests that these peaks are characteristic of MO. As for \(\lambda = 450\) nm, the peak intensity at \(t_R = 9.9\) min significantly decreased to a concentration order of ppm after the sample immersion (note that the intensity is magnified by a factor of 200 in Figure 4b for \(\lambda = 450\) nm). Several peaks at \(t_R = 7.6\) and 8.8 min were also detected after the immersion. Furthermore, as for \(\lambda = 210\) nm, the peak position remarkably shifted to shorter \(t_R\), accompanied with an increased peak intensity. It is generally accepted that the highly-polarized state of the analyzed compounds leads to shorter \(t_R\) in a reverse-phase HPLC. Hence, the polarity of the products in the solution after the immersion of nanoporous Au is higher than in the initial MO.

Furthermore, X-ray photoelectron spectroscopy on the sample before and after the immersion was conducted and the results are shown in Fig. S5. The Au 4f peaks were not shifted by the decoloration; thus the possibility of Au complex formation with the dye is eliminated.

Figures 3 and 4 demonstrate that nanoporous Au can catalytically reduce the MO concentration by chemical decomposition of MO and not by the simple adsorption of MO on the surface of the nanoporous Au, such as reported in the case of...
The fabrication of nanoporous metals other than Au has also been reported. In this study, nanoporous Pd (ligament size: 20 nm) and Ni (ligament size: 9 nm) are also fabricated by...
dealloying.\textsuperscript{58–41} (Fig. S3) and subjected to the MO degradation tests. As shown in Fig. 5, both nanoporous Pd and Ni clearly decreased the MO concentration in the surrounding solution. On the other hand, bulk Pd and Ni exhibited no decoloration of MO solution (Fig. S4). Thus, nanoporous Pd and Ni also can decolor MO solutions.

In summary, the concentration of an MO solution has firmly decreased by the simple immersion of nanoporous metals. The comparative experiments indicated that the atomically defective and strained surface, which are unique characteristics in nanoporous metals and alloys, have a significant effect on the MO decoloration. This catalysis needs no light irradiation unlike photocatalysts and is beneficial in the removal of textile industrial pollution, for example, in metallic channels which cannot permit light irradiation.

Acknowledgments

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Notes and references

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\textsuperscript{†} Electronic Supplementary Information (ESI) available: [Experimental details and additional results.] See DOI: 10.1039/b000000z.

5 P. Vivek and S. V. Rajender, Green Chem. 2010, 12, 743.
Electronic Supplementary Information

Catalytic decoloration of methyl orange solution by nanoporous metals

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1. Experimental details

Fabrication of nanoporous Au. A starting Au$_{0.3}$Ag$_{0.7}$ alloy sheet with thickness of 0.2 mm was fabricated by arc melting, homogenization annealing, cold rolling and cutting. Dealloying of the Au$_{0.3}$Ag$_{0.7}$ alloy sheet by free corrosion was conducted by immersion of the alloy sheet in 70 mass% HNO$_3$ at 263 K for 15 h (for Sample 1) and 298 K for 24 h (for Sample 2). Sample 3 was fabricated through electrochemical dealloying using the Au$_{0.3}$Ag$_{0.7}$ alloy sheet as a working electrode, that is, by electrolysis in 0.1 mol/L HNO$_3$ for 10 h at a potentiostatic condition of +1.1 V vs. a saturated calomel electrode (SCE) at room temperature.

Fabrication of nanoporous Pd. A starting Pd$_{0.2}$Co$_{0.8}$ alloy sheet was fabricated by arc melting, homogenization annealing, cold rolling and cutting. Electrolysis using the Pd$_{0.2}$Co$_{0.8}$ alloy sheet as a working electrode was conducted in 0.1 mol/L H$_2$SO$_4$ for 15 h at a potentiostatic condition at +0.5 V vs. SCE at room temperature.

Fabrication of nanoporous Ni. A starting Ni$_{0.3}$Mn$_{0.7}$ alloy sheet was fabricated by arc melting, homogenization annealing, cold rolling and cutting. Electrolysis using the Ni$_{0.3}$Mn$_{0.7}$ alloy sheet as a working electrode was conducted in 1 mol/L (NH$_4$)$_2$SO$_4$ aqueous solution for 10 h at a potentiostatic condition at −0.65 V vs. SCE at room temperature.

Characterization. Samples were observed using a field-emission scanning electron microscope (FE-SEM, SU6600 by Hitachi High-Technology Corp.) equipped with
energy-dispersive X-ray spectroscopy (EDXS). The roughness factor of the nanoporous Au samples, which is the ratio of the electrochemically active surface area of nanoporous Au to that of smooth Au, was estimated using the charge associated with the reduction of adsorbed oxygen during cyclic voltammetry in 0.1 mol/L H₂SO₄ (Trasatti and Petrii, *J. Electroanal Chem.* 327 (1992) 353).

**High-performance liquid chromatography (HPLC).** Target solutions (10 µL) were analyzed using HPLC. Columns of Shim-pack VP-ODS with length of 150 mm and inner diameter of 4.6 mm were employed. The mobile phase was composed of two components; one is 10 mmol/L sodium phosphate buffer solution (pH 2.6) with 100 mmol/L sodium perchlorate and the other is acetonitrile. Gradient analysis at 313 K with a flow rate of 0.8 mL/min was conducted according to the concentration schedule shown in Table S1.

### Table S1. Concentration schedule for HPLC.

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Concentration of acetonitrile (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>5</td>
</tr>
<tr>
<td>10.00</td>
<td>70</td>
</tr>
<tr>
<td>15.00</td>
<td>70</td>
</tr>
<tr>
<td>15.01</td>
<td>5</td>
</tr>
<tr>
<td>22.00</td>
<td>Stop</td>
</tr>
</tbody>
</table>
2. Additional results

**Immersion of TiO$_2$ and ZnO sheets.** Figure S1 shows the time variation of methyl orange (MO) concentration after immersion of TiO$_2$ and ZnO sheets in the MO solution under a dark condition. No decrease in MO concentration was detected. This is due to the absence of light irradiation, because photocatalytic TiO$_2$ and ZnO require light for decomposition of MO.

![Figure S1](image)

**Figure S1.** Time variation of methyl orange concentration after the immersion of TiO$_2$ and ZnO sheets under a dark condition.

**Logarithmic decrease in MO concentration by nanoporous Au.** Figure S2 shows the logarithmic decrease in MO concentration after the immersion of nanoporous Au samples in the MO solution. The plots are well represented along the straight lines. This suggests that first-order reaction kinetics is reasonable for the MO decomposition.
Figure S2. Time variation of MO concentration after the immersion of nanoporous Au samples in the MO solution measured according to a logarithmic scale. The numbers indicate the Sample No. presented in Table 1.

SEM images of nanoporous Pd and Ni. Figure S3 shows the SEM images of nanoporous Pd and Ni. Ligament sizes of 20 and 9 nm were observed in nanoporous Pd and Ni, respectively.

Figure S3. SEM images of nanoporous Pd and Ni.
**Immersion of bulk Pd and Ni sheets.** Figure S4 shows the MO solution after 120-h immersion of bulk Pd and Ni sheets as well as control run (without sample immersion). Bulk Pd and Ni exhibited no decoloration of MO solution.

![Figure S4. MO solution (initial concentration of $2 \times 10^{-5}$ mol/L) after 120-h immersion of bulk Pd and Ni sheets. Bulk Pd and Ni exhibited no decoloration on MO solution.](image)

**XPS analyses.** Figure S5 shows the X-ray photoelectron spectra of nanoporous Au (sample 1) before and after MO decoloration. The Au 4f peaks were not shifted by the decoloration, indicating that Au complex with the dye does not form.

![Figure S5. X-ray photoelectron spectra of nanoporous Au (sample 1) before and after MO decoloration.](image)