Patterning of Gold and Gold Black Electrode Surfaces by Photocatalytic Lithography

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Introduction

Micropatterning of electrode surfaces in terms of functionality or chemical affinity is an important technology for the development of advanced modified electrodes and devices like a biochip and lab-on-a-chip. In the present work, we applied "photocatalytic lithography",[1-3] which we have developed on the basis of photocatalytic remote oxidation,[4] to micropatterning of gold and gold black electrode surfaces.

Experimental

A gold thin film as the substrate electrode was deposited on a Pyrex glass plate by sputtering. The gold film was polarized at -0.08 V vs. Ag|AgCl in an aqueous solution containing 50 mM tetrachloroaurate and 5 mM lead acetate for 5 min to modify the electrode surface with gold black. These gold and gold black electrodes were immersed in an ethanolic solution of 10 mM thiol for 1 h to form a self-assembled monolayer (SAM) of the thiol on the electrodes. A photomask coated with a TiO_2 photocatalyst was located on these gold and gold black electrodes with a 12.5 μm thick Kapton spacer (Figure 1). As the TiO_2 film was irradiated with UV light (100 mW/cm^2) through the photomask, a two-dimensional pattern corresponding to the mask was transferred onto the SAM on the gold or gold black electrode.

Results and discussion

The contact angle for water of these SAM-modified gold electrodes depended on the endgroups of the thiol used. When the endgroup was carboxylic or amino group the electrode surfaces were hydrophilic. On the other hand, in the case of an alkyl (octane thiol: OT) or fluoroalkyl (1H,1H,2H,2H-perfluorodecanthiol: PFDT) groups, the electrode surfaces were hydorophobic. After the photocatalytic treatment, the water contact angle of these hydrophobic electrodes slightly decreased, that is, hydrophobicity decreased.

X-ray photoelectron spectrometry (XPS) measurements of the OT-modified gold electrodes revealed that the amount of carbon decreased while the amount of oxygen increased during the photocatalytic treatment. After the amount of carbon decreased to a constant value, conversion of mercaptan to SO_2 started. On the basis of these results, we can conclude that the SAM was decomposed gradually from the endgroups.

The OT-modified gold surface was patterned by means of photocatalytic lithography. The hydrophilic/hydrophobic patterns were visualized by using water vapor or rhodamin 6G. A line of 20 μm thick could be patterned. However, the contrast was not sufficient.

In the case of the gold black electrode, of which surface was roughened in the submicrometer scale, hydrophobicity of the OT- or PFDT-modified surface and hydrophilicity of the bare and carboxylate- or amino-modified surfaces were enhanced in comparison with those of the smooth gold electrode surfaces (Table 1). These effects can be explained in terms of Wenzel equation. Especially, the PFDT-modified gold black electrode surface was super-hydrophobic (water contact angle >150°). The surface was converted to super-hydrophilic (water contact angle ~ 0°) by the photocatalytic treatment. Thus, the contrast in hydrophilic/hydrophobic patterns obtained by photocatalytic lithography was enhanced at the gold black electrode surface.

Next, we examined the patterning with enzyme peroxidase. Peroxidase was successfully immobilized only in the hydrophilized regions on the patterned gold black electrode surface. Although the resolution is currently on the order of mm, the work is underway to improve it to the order of μm.

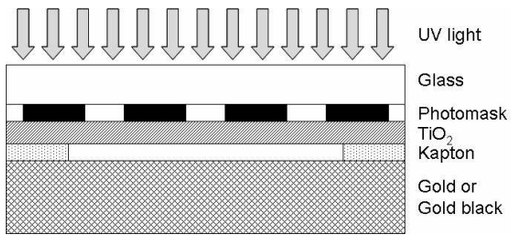

Fig. 1 Experimental setups for the photocatalytic lithography based on the remote oxidation.

Table 1 Water contact angles of thiol SAM-modified gold and gold black electrodes.

	Water contact angle / degree			
Substrate	OT	PFDT	AET	After photocatalytic Treatment (PFDT)
Gold	110	115	30	100
Gold black	120	>150	5	5

OT: Octanethiol
PFDT: 1H,1H,2H,2H-Perfluorodecanethiol
AET: Aminoethanethiol

References
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