

AN APPLICATION OF PHOTOELECTROCHEMICAL DEPOSITION OF
HYDROPHOBIC ORGANIC LAYERS ON SEMICONDUCTOR ELECTRODES
TO IMAGING SYSTEMS

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Photoelectrochemical oxidation of aromatic compounds on semiconductor electrodes was applied to an imaging system. Change of hydrophilic and hydrophobic properties (wettability) of the surface of the semiconductor electrodes accompanied with organic layer deposition was studied by measuring the contact angle and its applicability to imaging systems was evaluated.

There has been a considerable interest in photoelectrochemical imaging systems employing redox reactions on semiconductor electrodes in connection with applications in display devices,^{1,2)} printing systems³⁾ and semiconductor microelectronic processes.⁴⁾ Photoelectrochemical imaging has several advantages such as reversibility, low electric power drivability and simplicity of use.

We have studied change in the hydrophilic and hydrophobic properties (wettability) of the surfaces of semiconductor electrodes accompanied with photoelectrochemical oxidation of aromatic compounds and developed a new type of photoelectrochemical imaging system. Once the hydrophilic surfaces of n-type semiconductor electrodes were covered with organic layers deposited, they changed markedly from hydrophilic to hydrophobic. As the deposition of the organic layer occurred in only illuminated regions of the semiconductor electrode, a hydrophobic image on the hydrophilic surface was obtained corresponding to the illumination pattern. This image could be developed by water color or oily color ink and resulted in a visible image as demonstrated in Fig. 1. Since the very thin layer of aromatic compounds displayed hydrophobicity enough for the development, imaging of high sensitivity was attained. The electrochemical or photoelectrochemical formation of organic layers has been extensively investigated in electrocatalysis⁵⁾ and anticorrosion of electrodes.⁶⁾ However, few studies have been done on the hydrophilic and hydrophobic properties of electrode surfaces^{7,8)} and no work has been reported on their applicability to imaging systems.

Polycrystalline TiO_2 was used as a semiconductor electrode here, since its surface was hydrophilic satisfactory in clean condition and stable to anodic polarization. The TiO_2 electrode was prepared by oxidizing a titanium plate (0.2 mm in thickness) in a gas burner for 5 min following the procedure reported in Ref. 9. The electrochemical oxidation was carried out by anodic polarization

in a 0.2 M (1 M = 1 mol dm⁻³) Na₂SO₄ aqueous solution containing a water soluble aromatic compounds, simultaneously illuminated with a light from a 150 W Xe arc lamp (Varian) with a glass filter (Toshiba UVD2, $\lambda_{\text{max}} = 360$ nm). For electrochemical measurements, a potentiostat (Toho Giken 2000) was used and all potentials were measured with a calomel reference electrode. Evaluation

of wettability was performed by measuring the contact angle of a drop water deposited on the surface of the electrode using a contact angle meter (Kyowa Kagaku). The thickness of the deposited layer was measured with a surface profile meter (Sloan Dektak).

In Table 1, the contact angles of the TiO₂ electrode after the photoelectrolysis in the aqueous electrolytes containing various aromatic compounds are summarized. The compounds shown in Table 1 are known to be polymerized by anodic oxidation and form stable films on electrode surfaces. Other water soluble aromatic compounds such as benzoic acid and benzaldehyde showed only a slight increase of contact angle. In what follows, the behavior of the oxidation of o-toluidine will be illustrated in some detail.

Figure 2 shows typical changes in the contact angle plotted against time along with a photocurrent for the electrolysis with and without illumination. The contact angle in the illuminated area increased steeply with time and attained a saturated value, while the contact angle in the dark area showed a slight increase which was assumed to be due to partial adsorption of the o-toluidine molecules on the surface. The photocurrent remained almost constant throughout the experimental period in Fig. 2. It implies that the charge transfer is not disturbed by the change in hydrophilicity of the surface in the thin layer deposition. The thickness of the deposited layer was evaluated to be 110 Å at the saturated point on the basis of the charge passed. The value of the charge corresponding to a specific thickness (18 mC/cm² per 1000 Å) was obtained using a Au evaporated electrode of which the surface was smooth and suited for surface profile measurement. As for the imaging, the deposition of the layer less than 30 Å in thickness brought about the hydrophobic

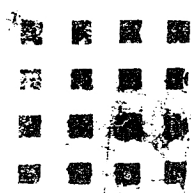


Fig. 1. Photograph of oily color ink image obtained by TiO₂/o-toluidine system. TiO₂ electrode (5 cm x 4 cm) was photoelectrolyzed at 1 V vs. SCE in 0.1 M o-toluidine solution with illumination (6 mJ/cm²). After the oily color inking, the image was transported to plane paper.

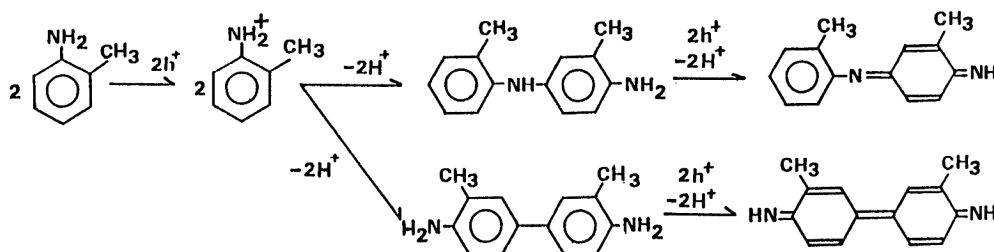
Table 1. Contact angle of TiO₂ electrode after photoelectrolysis (20 mC/cm²) in aqueous solution containing aromatic compounds

Aromatic compounds	Contact angle (DEG)
Aniline ^{a)}	58 ± 4
o-Toluidine ^{a)}	69 ± 4
p-Aminobenzoic acid ^{b)}	30 ± 3
Phenol ^{a)}	43 ± 8
o-Cresol ^{a)}	60 ± 8
m-Aminophenol ^{a)}	37 ± 5

a) 0.1 M. b) 0.02 M.

image which could be developed by the inking treatment. These results indicate that the surface covered with the very thin organic layer displays the good hydrophobicity. This property of the hydrophobicity change contributes to the high sensitivity of the imaging system.

The rate of change in the contact angle depended on a quantum efficiency of the photoanode. Figure 3 shows the dependence of the change in the contact angle on the irradiation wavelength. The action spectrum of the change agreed with that of photocurrent efficiency. In the case of measuring the dependence of the rate of contact angle change on applied potentials, the maximal rate was observed at the potential which gave the saturated photocurrent. From these results, it was confirmed that the formation of the hydrophobic layer was caused by anodic oxidation of the aromatic compounds due to the photoexcited holes in the TiO_2 electrode. Based on the reaction mechanism by Desideri et al.,¹⁰⁾ the scheme is illustrated as follows:



However, it is also possible that intermediates (e.g. $\text{OH}\cdot$ radicals) formed during the photoelectrolysis play an important role in the initial step of the oxidation process, considering the results reported on TiO_2 /aqueous medium systems.¹¹⁾

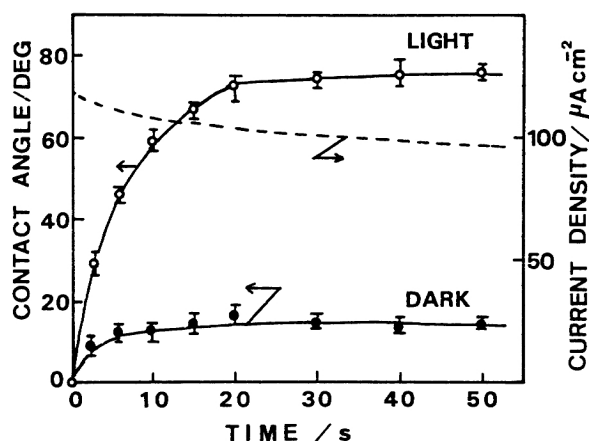


Fig. 2. Contact angle and photocurrent versus time curves for TiO_2 electrode. Solution: 0.1 M o-toluidine and 0.2 M Na_2SO_4 (PH 5). $E = +1.0$ V vs. SCE. Light intensity = 1 mW/cm^2 .

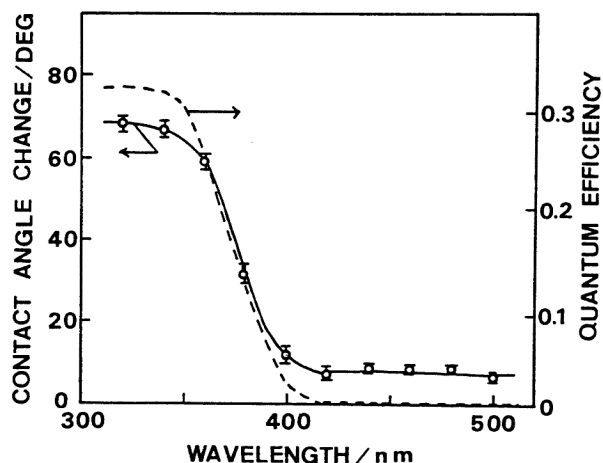


Fig. 3. Dependence of contact angle change on the irradiation wavelength. Solution: The same as in Fig. 2. Incident photon number = $1.6 \times 10^{16}/\text{cm}^2$.

The other aromatic compounds in Table 1 showed similar behavior to that observed for the o-toluidine. The hydrophobic layers adhered strongly to the surface and were stable in air. The reversibility of the imaging system was not good, because the hydrophobic layers could not be removed by cathodic polarization of the TiO_2 electrode. However, the layer could be removed by high anodic polarization (greater than 3.0 V vs. SCE). When the TiO_2 electrode was subjected to high anodic polarization, dark current due to the tunneling process appeared and the deposited layer was oxidized and destroyed. Though the mechanism accounting for the removal of the layer is not clear at the present stage, the photoreceptor (TiO_2 electrode) was reproduced through this treatment and repeated utilization of the imaging system was achieved.

It was demonstrated that a hydrophobic image could be effectively obtained by photoelectrochemical oxidation of the aromatic compounds. This imaging system has high sensitivity and may be applicable to various printing systems e.g. off-set planography.

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