Mechanisms of Photocatalytic Remote Oxidation and Application to Photocatalytic Lithography

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Introduction

The photocatalytic remote oxidation of organic and inorganic compounds via the gas phase was studied in detail. In the remote oxidation, active oxygen species (AOS) diffuse from TiO_2 via the gas phase and oxidize various organic and inorganic compounds.[1] We have also applied the remote oxidation to photocatalytic lithography.[2,3]

In our previous work, we found that a strong oxidizing species like ·OH and a double excitation mechanism are involved in the remote oxidation.[3] On the basis of these results, we proposed possible mechanisms of the remote oxidation in which photocatalytically generated H_2O_2 diffuses via the gas phase and is photo-decomposed into ·OH. In present work, we examined whether H_2O_2 is involved in the remote oxidation. Also, the patterning technique based on the photocatalytic lithography was further developed.

Experimental

A glass plate treated with octadecyltriethoxy-silane (ODS) or heptadecafluorodecyltriethoxy-silane (HDFS) was used as a probe for the remote oxidation. The plate was faced to a TiO_2 coating with a small intervening gap (12.5 μm). The TiO_2 coating was irradiated with UV light from its back. The area exposed to UV light was degraded and become hydrophilic. TiO_2-coated photomasks were used for the patterning based on photocatalytic lithography (Fig. 1).

For the detection of H_2O_2 released from TiO_2, a flow-through cell as shown in Fig.2 was prepared.

Results and Discussion

First, we have tried to detect H_2O_2 released from TiO_2 to air by using the TiO_2 cell (Fig.2). After UV irradiation for 1 h, $(6.3 \pm 1.2) \times 10^{-10}$ mol of H_2O_2 was detected, while no H_2O_2 was detected in the absence of TiO_2.[4] These results are in line with the mechanisms we proposed.

Next, we comprised the remote oxidation with the gaseous H_2O_2-UV reaction. If the photo-decomposition of gaseous H_2O_2 into ·OH is involved in the remote oxidation, those two reactions should exhibit similar behavior. Actually, both of the remote oxidation and the gaseous H_2O_2-UV reaction converted the surfaces of the ODS-coated and HDFS-coated glass plates, which were initially hydrophobic, to hydrophilic. Namely, ODS and HDFS are decomposed by the H_2O_2-UV reaction as well as the remote oxidation. Although all these results are in consistent with the proposed mechanisms, we cannot yet conclude that the remote oxidation involves H_2O_2. To provide clearer evidences, we will examine action spectra of the reactions.

Next we applied the remote oxidation to surface modification and patterning. We have prepared a microstructured silica surface, and modified it with ODS to obtain a super-hydrophobic surface with water contact angle of 151°. This surface was converted to super-hydrophilic (water contact angle < 5°) by the remote oxidation. Also, the super-hydrophobic surface could be patterned by means of photocatalytic lighography (Fig. 3).[5]

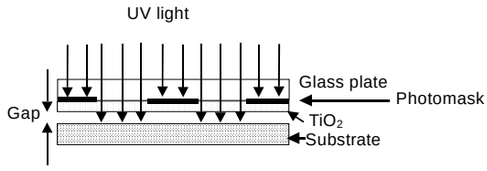

Fig. 1 Experimental setup for the photocatalytic lithography.

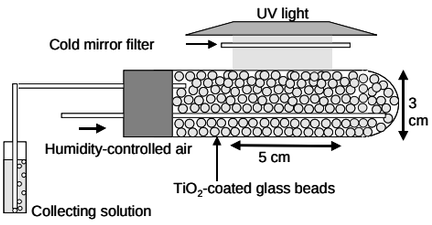

Fig. 2 Experimental setup for the detection of H_2O_2.

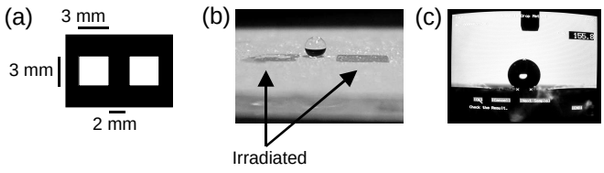

Fig. 3 Diagram of (a) the TiO_2-coated photomask used and (b, c) photographs of the ODS-modified SiO_2 microparticle film surface patterned by photocatalytic lithography with the photomask (5 min irradiation) and water dropped on the irradiated and non-irradiated regions.

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2. T. Tatsuma, W. Kubo, A. Fujishima, *Lungmuir*, **18**, 9632-9634 (2002).
3. W. Kubo, T. Tatsuma, A. Fujishima, and H. Kobayashi, *J. Phys. Chem. B*, **108**, 3005 (2004).
4. W. Kubo and T. Tatsuma, *Anal. Sci.*, **20**, 519 (2004).
5. W. Kubo and T. Tatsuma, submitted.