Surface Asymmetrization for Efficiency Increase in Nano-sized TiO_2 Photocatalysts

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Nano-crystalline TiO_2 or related metal-oxide photocatalysts have been attracting strong attention as a promising approach to low-cost solar energy conversion and environmental cleaning. Recently, this technique has prompted new interest by the finding that doping of metal oxides with nitrogen, sulfur, carbon, or other elements leads to an extension of the photoactive area from the UV to visible-light region. The remaining important problem to be solved is now how to increase low quantum efficiencies that inevitably arise from the lack of band bending in particulate systems. In the present paper, we report that photoetching of nano-sized TiO_2 (rutile) particles can introduce the surface asymmetry (i.e. band bending) and provides a novel powerful approach to solve the above problem.

Figure 1 schematically shows the effect of the band bending (or band inclination) on the photoreaction efficiency for (1) insulating and (2) semiconducting metal-oxide particles. If the particles have homogeneous uniform surfaces, the band energies are flat all over the surface and in the interior (A-1 and A-2). In such a case, photogenerated charge carriers (electrons and holes) diffuse randomly within the particles and thus easily recombine with each other. On the other hand, if the particles have asymmetrized surfaces, introduced by a certain surface treatment, and have different surface band energies at different parts of the surface, the band bending (inclination) is introduced in the interior of the particles (B-1 and B-2). In this case, the band bending causes effective separation of photogenerated charge carriers, thus leading to a large increase in the quantum efficiency of photocatalytic reactions.

The remaining problem is how to introduce the surface asymmetry into a huge number of extremely small (nano-sized) photocatalyst particles, existing in the form of thin films or suspension. To date, we have had no effective way to introduce the surface asymmetry in such systems. Recently, we have found that directional and face-selective photoetching that occurs[1,2] for TiO_2 (rutile) in aqueous H_2SO_4 can be used for introducing the surface asymmetry into the TiO_2 (rutile) particles. The important points of our findings are (1) the photoetching proceeds in the <001> direction, with the (100) face selectively exposed at the etched surface[1,2], (2) similar photoetching proceeds also for suspended TiO_2 (rutile) particles with Pt dots[3], and (3) the flat-band potential, U_{fb} for the (100) face is about 0.09 V more negative than that for the (110) face[4]. Thus, partial photoetching results in etched and non-etched parts at the surface of TiO_2 particles, with different U_{fb}. Namely, the partial photoetching introduces the surface asymmetry.

Our recent experiments have shown[4] that the surface asymmetrization actually leads to a large increase in the photoreaction efficiency (Fig. 2), clearly indicating that it is a powerful way to increase the efficiency in particulate photocatalyst systems.

References

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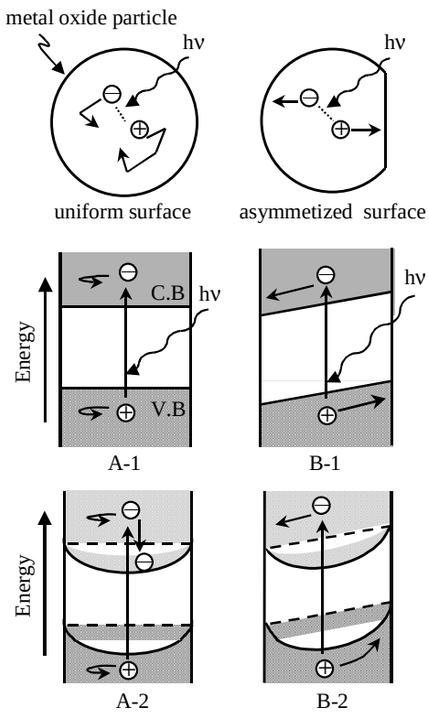

Fig. 1 Schematic illustration of the effect of the band bending on the photoreaction efficiency for (1) insulating and (2) n-type semiconducting metal-oxide particles.

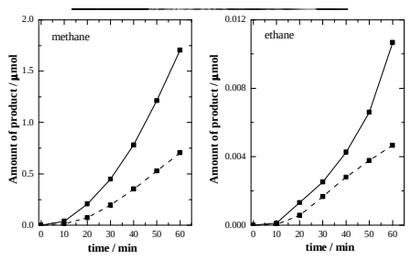

Fig. 2 The amounts of photo-products (methane and ethane) of photo-Kolbe reaction on the (solid curve) photoetched and (broken curve) non-photoetched TiO_2 particles, as a function of the illumination time.