—Note—

Acceleration of Photocatalytic Antibacterial Action of TiO_2 by Halide Ions against Oral Microorganism

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1 INTRODUCTION

The photocatalytic activity of semiconductor powders has been investigated in such heterogeneous photocatalytic processes as hydrogen production from water[1], decomposition of waste organic chemicals[2], reduction of carbon dioxide[3], various organic chemical syntheses[4] and bactericidal action against some bacterial species[5].

We have communicated that powdered TiO_2 semiconductor has a photocatalytic effect on dental plaque and inhibits the viability of *Streptococcus mutans*, when reaction mixtures are irradiated with UV light[6,7].

In the present paper, we describe the prominent acceleration of photocatalytic antibacterial action of powdered TiO_2 semiconductor by some halide ions against oral microorganism.

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2 EXPERIMENTAL

Experiments were made with the fine-grain TiO_2 particle (P-25, Nippon Aerosil Co., LTD.) which is composed of 70% anatase and 30% rutile.

The stationary culture of *S.mutans FA-1* was carried out in Brain Heart Infusion broth (BHI broth, Difco Lab.) at 37℃ for 24 hours. The culture ($5\times10^{-3}cm^3$) was suspended in 100 cm^3 of an aqueous solution of halides containing 0.1% TiO_2 by weight.

For the experiment of photocatalytic antibacterial effect, a glass vessel with bacterial suspension was set 5 cm apart from the light source and irradiated with a fluorescent lamp (FL20S-BL, Toshiba Corp.).

The viable cell count was measured by counting the colonies with a smear method using BHI agar.

3 RESULTS AND DISCUSSION

In the previous paper[6], we have demonstrated the following conclusions, (1) photoexcited surface on powdered TiO_2 semiconductor contacted with a liquid phase has an excellent bactericidal capacity against *S.mutans* which is one of oral microorganisms, (2) the photocatalytic antibacterial action is more effective under near-ultraviolet irradiation than under visible one, (3) in this effect, anatase TiO_2 is superior to rutile TiO_2 .

Here we report that the photocatalytic

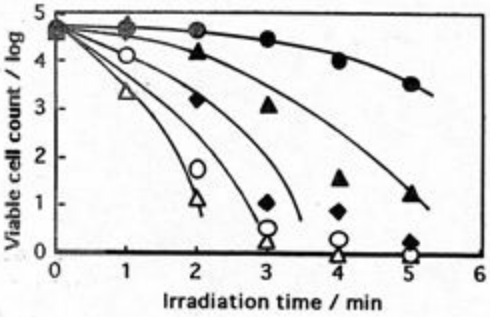

Fig.1 Photocatalytic antibacterial action against *S.mutans* in bacterial suspension with sodium chloride.

Concentration of sodium chloride/ mol · dm^{-3}

●: 0.03, ▲:0.05, ◆:0.1, ○: 0.2, △: 0.3.

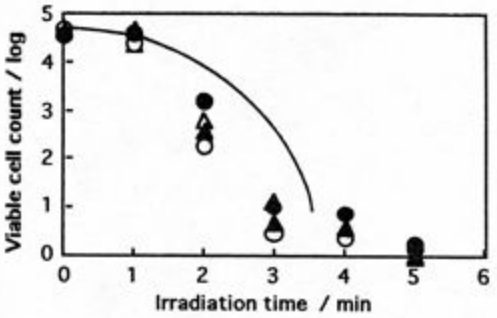

Fig.2 The influence of counter ions on photocatalytic antibacterial action of chloride.

●: 0.1mol · dm^{-3} NaCl,

▲: 0.1mol · dm^{-3} KCl,

○: 0.05mol · dm^{-3} $MgCl_2$,

△: 0.05mol · dm^{-3} $CaCl_2$.

antibacterial action can be accelerated by halide ions in bacterial suspension. As is shown in Fig.1, the inhibitory effect on the viability of *S.mutans* was observed when bacterial suspension containing TiO_2 was irradiated with near-UV light.

In the figure the time required for photocatalytic antibacterial effect became markedly short with increasing concentration of sodium chloride in bacterial suspension.

In either control experiment without light or powdered TiO_2, no inhibitory effect was observed on the viability of *S.mutans*. As is shown in Fig.2, the accelerative effect of chloride ion on photocatalytic antibacterial action was not influenced by counter ions, such as Na^+, K^+, Ca^{++} or Mg^{++}, paired with chloride anion. Conversely in Fig.3, the dependency of the accelerative effect on the kind of halide ion derived the following features; (1) fluoride ion alone has no accelerative effect, (2) bromide ion is the most effective to the accelerative effect, (3) iodide ion is as effective as chloride ion. Those halide ions which accelerated the photocatalytic antibacterial action can be oxidized more easily than water according to their electrochemical oxidation potentials.

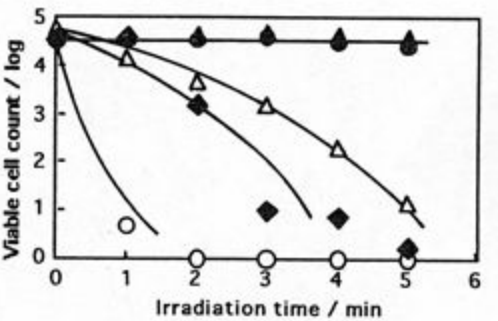

Fig.3 The effect of halide ions on photocatalytic antibacterial action.

●: distilled water,

▲: 0.1mol · dm^{-3} NaF,

◆: 0.1mol · dm^{-3} NaCl,

○: 0.1mol · dm^{-3} NaBr,

△: 0.1mol · dm^{-3} NaI.

Therefore the acceleration effect, although the mechanism is still uncertain, may be attributed to the production of antibacterioactive species in the course of oxidation process of halide ions on TiO_2 surface.

Present results will suggest the possibility of usage of powdered TiO_2 especially in dentistry.

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