

Fundamental Study on Activation Mechanism of Titanium Dioxide Composite Irradiated by Low-Intensity Focused Ultrasound

低強度集束超音波による酸化チタン複合体の活性機序に関する基礎検討

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1. Introduction

It is well known that OH radical is produced by irradiating ultraviolet to titanium dioxide as photocatalyst, and that effect is used for removing harmful material such as organic compounds and bacteria in the environmental field. Recently, ultrasound is also used as stimulus source of titanium dioxide, and it is reported that the ultrasound irradiation with frequency of several kHz can kill some coliform¹⁾.

On the other hand, in the medical field, the exit site infection of catheter retained in the body has become a serious problem. We are developing a novel method of infection prevention, that the exit site of catheter is covered with the titanium dioxide composite²⁾, which is the silicone sheet coated by the aminated titanium dioxide (AmTiO₂) nanoparticle, and then OH radical for sterilization is generated by irradiating low-intensity focused ultrasound (LIFU) to the AmTiO₂ on the exit site of catheter³⁾.

In this study, OH radical production by LIFU irradiation to AmTiO₂ is confirmed and the activation mechanism of TiO₂ composite is investigated through dye decomposition experiment.

2. OH Radical Production by LIFU Irradiation

Figure 1 shows an experimental setup for confirming OH radical production by LIFU irradiation. A sample tank, whose bottom is covered with aminated titanium dioxide composite sheet, is filled with salicylic acid solution (0.1 mM, 10mL). Ultrasound (500 kHz, CW) is irradiated to the bottom of the sample tank during 60 minutes. The used intensities are 0.6 W/cm² below 1 W/cm² and 1.5 W/cm² beyond 1 W/cm² as safety limit. Irradiated salicylic acid solution is analyzed by the high-performance liquid chromatography (HPLC).

Figure 2 shows the obtained chromatograms in each ultrasound intensity. Figure 2(a) indicates

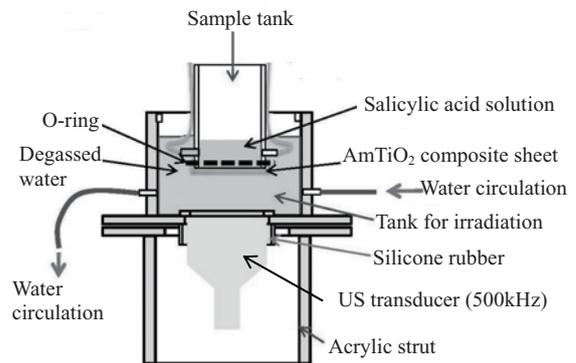
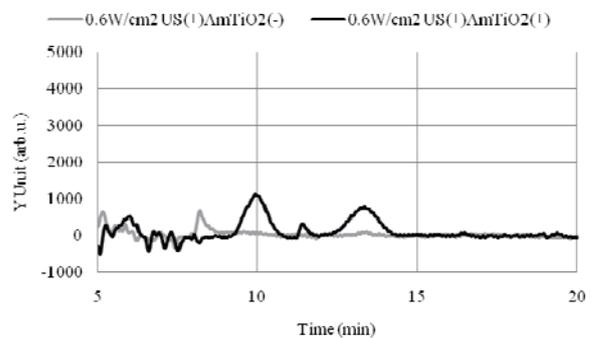
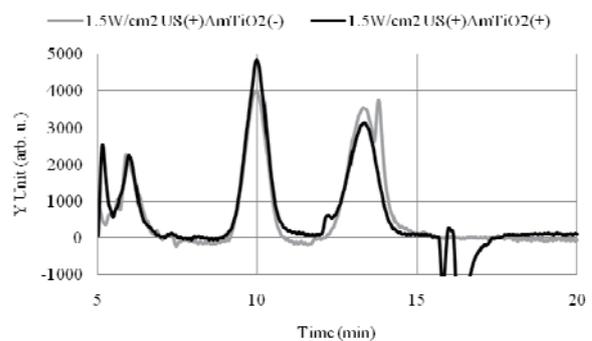


Fig.1 Experimental setup for OH radical production.



(a)



(b)

Fig.2 Chromatograms indicating OH radical production by LIFU on titanium dioxide composite.

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OH radical production even if the low-intensity ultrasound below safety limit is irradiated to titanium dioxide. On the other hand, OH radical is not produced when there is no titanium dioxide. Figure 2(b) indicates significant OH radical productions in both cases because the irradiation intensity is beyond safety limit and the cavitations occur.

3. Mechanism Investigation of TiO₂ Activation by LIFU

In Fig.2(a), we observed that the OH radical is produced even if the low-intensity ultrasound below safety limit is irradiated to titanium dioxide. As the reason of this phenomenon, we presume that the cavitation threshold decreases under the existence of titanium dioxide nanoparticle, in an analogous way of microbubble effect. Therefore, we conducted dye decomposition experiment with methylene blue solution and evaluated the dye decomposition threshold⁴⁾. Here, we hypothesize the dye decomposition threshold correlates with the cavitation threshold.

Dye decomposition experiments were conducted by using the setup of Fig.1. Sample tank is filled with the methylene blue solution and the ultrasound was irradiated from the bottom of the tank. Two samples of methylene blue solution with and without TiO₂ nanoparticle were prepared. Input voltage to ultrasound transducer were changed from 0 to 50 V during 60 minutes. And then, the change of absorbance was measured by using a spectrophotometer. Figure 5 shows the change of absorbance for obtaining dye decomposition threshold. These measured points were approximated by the linear line and the intersection of x axis was obtained. That is, the intersection corresponds to the dye decomposition threshold.

Obtained dye decomposition thresholds are shown in Fig.6. Here, the input voltage is converted into the intensity. Since the dye decomposition threshold in the methylene blue solution with TiO₂ nanoparticle decreased significantly, the decrease of cavitation threshold in the methylene blue solution with TiO₂ nanoparticle is also predicted. As the result, we also predict that the cavitation occurs in the limited region on the titanium dioxide composite sheet even if the safety ultrasound intensity is used, and OH radical is produced.

On the other hand, in the OH radical production, the photocatalyst effect of titanium dioxide is needed to investigate as future work. In the photocatalyst effect of titanium dioxide, although the OH radical is produced by irradiating ultraviolet to the titanium dioxide, this contribution is needed to reveal in the ultrasound irradiation method.

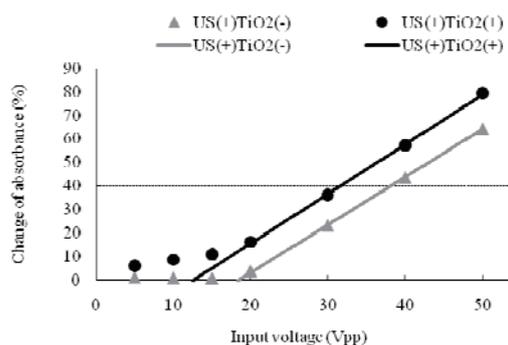


Fig.3 Change of absorbance for obtaining dye decomposition threshold.

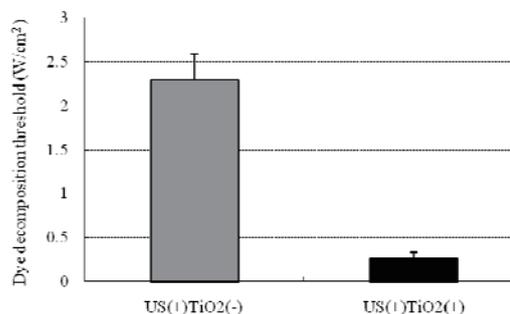


Fig.4 Comparison of dye decomposition threshold.

4. Conclusion

In this study, we are developing a novel method of infection prevention, that the exit site of catheter is covered with the titanium dioxide composite, which is the silicone sheet coated by the aminated titanium dioxide nanoparticle, and then OH radical for sterilization is generated by irradiating low-intensity focused ultrasound to the TiO₂ on the exit site of catheter. Experimental results indicate the possibility that a trigger of TiO₂ activation by low-intensity ultrasound irradiation is the cavitation threshold decrease. In future work, the influence of photocatalyst effect of titanium dioxide will be investigated.

References

1. N. Shimizu et al.: *Chouonpa Riyou Gijutsu Syuusei*, NTS, Tokyo (2005) 115.
2. M. Okada et al.: *J. Biomed. Mater. Res.* **76A** (2006) 95.
3. N. Nitta et al.: *Proc of Research Committee of Acoustic Imaging AI2008-4-5* (2008) p.24.
4. K. Okada et al.: *Proc of USE 2008* **29** (2008) pp.419.