Journal of Photoscience (2002), Vol. 9(2), pp. 409–411

A Generator of Gaseous Singlet Oxygen

Teruo Matsuura[1]*, Hideya Sato[2], Nobutaka Suzuki[3] and Masakatsu Matsumoto[4]

[1] Emeritus Prof., Kyoto University, 21-26 Kawashima-Gondencho, Saikyoku, Kyoto 615-8195, Japan

[2] Optec, Ltd., 5-43-8 Oshima, kotoku, Tokyo 136-0072, Japan

[3] Department of Food Chemistry, National University of Fisheries, Shimonoseki 759-6595, Japan

[4] Department of Material Science, Kanagawa Univerdity, hiratsuka 259-1205, Japan

In order to prevent side reactions due to free radical formation occurring in the reactions of singlet oxygen generated in solution phse, it was required that singlet oxygen is generated in gas phase from an apparatus of a solid-gas system. We have accomplished to construct an apparatus generating singlet oxygen in solid-gas system, which is composed of a flexible optical fibre tube connected by a dye-sensitizer probe containing rose bengal dye on polymer or inorganic material. Through the optical fibre tube visible light from a laser and an oxygen stream are passed into the sensitizer probe where singlet oxygen is generated. The determination of singlet oxygen was carried out by two methods. One involves the detection of the luminescence of singlet oxygen at 1268 nm and the other involves the chemiluminescence reaction of a dihydroisobenzofuran with singlet oxygen emitting luminescence at 456 nm.

Key words: singlet oxygen generator, dye sensitized oxygenation, luminescence、chemiluminescence

INTRODUCTION

Singlet oxygen, an electronically excited state of oxygen is known to play important roles in the dye-sensitied photooxygenation of biological systems [1]. There are many types of methods generating singlet oxygen [2], but the methods usually done in solution phase and some side reactions due to free radical formation inevitably occur. Because of its short life time, it is required that singlet oxygen is generated in gaseous phase from an apparatus consisting of a solid-gas system but not a solution system. Thus, when a dye-sensitizer solution is irradiated with visible light under oxygen bubbling, no singlet oxygen will be found in the exhausted gas. Therefore, we attempted to construct an apparatus generating singlet oxygen in solid-gas system.

* To whom correspondence should be addressed.

E-mail: mats303@attglobal.net

MATERIALS AND METHOD

Reagents — Dye sensitizers, including rose bengal and phthalocyanine, organic solvents and other chemicals were commercially avaiable.

Construction of singlet oxygen generator — The outline of the generator is illustrated in Figure 1. The generator consisted of a light source, an argon laser or a metal halide lamp, two infrared cut filters, optical fiber surrounded by a flexible metal tube and attached an oxygen gas inlet , a dye sensitizer probe, a glass receiver for singlet oxygen gas outlet and a singlet oxygen detector (DET). The dye sensitizer probe is replaceable and contains a dye sensitizer, such as rose bengal and phthalocyanine, adsorbed on porous organic or inorganic resin.

RESULTS AND DISCUSSION

Determination of singlet oxygen — Determination was carried out by the following two methods.

(1) Direct mesurement of the luminescence of singlet oxygen: Singlet oxygen is known to emit luminescence in several ways and the luminescence at 1268 nm is commonly employed for measurements. For the determination of the luminescence of singlet oxygen, we employed two kinds of ultra-high sensitive instruments, trans-impedance amplifier and charge integrating amplifier systems [3]. The spectrum, obtained using the standard rose bengal probe under irradiation with an argon laser (514 nm; 79.8 mW) with the oxygen flow speed of 8 sccm (6.2ml / min), is shown in Fig.2 indicating the formation of singlet oxygen.

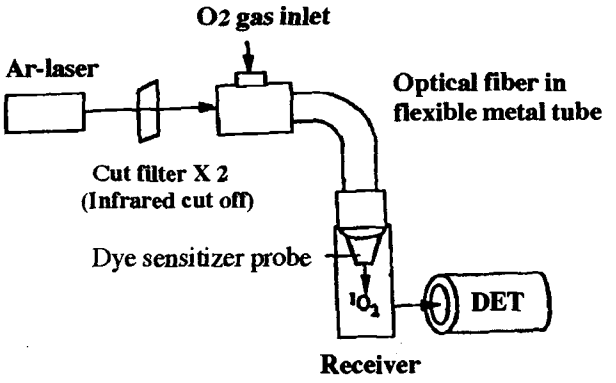


Fig. 1. Outline of the singlet oxygen generator.

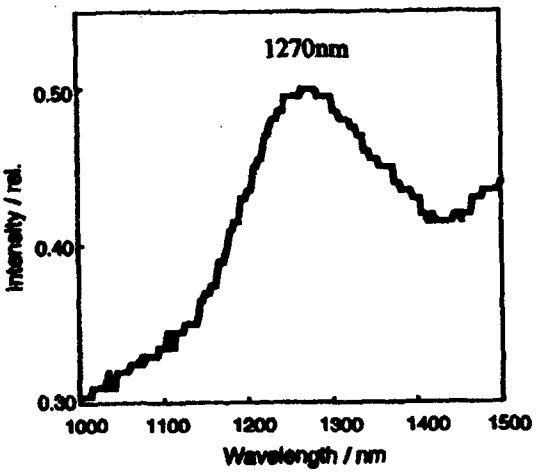
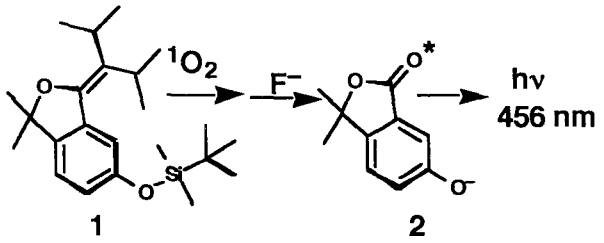


Fig. 2. Luminescence of singlet oxygen at 1268 nm.

The peak intensity of the luminescence of singlet oxygen is depending upon the shape of dye-sensitizer probes. We also found that peak intensity was highly dependent upon the distance between the outlet of the dye-sensitizer probe and the position of the detector of singlet oxygen luminescence. The peak intensity became smaller when this distance became longer. The result indicates the short lifetime of singlet oxygen under the conditions particularly under the atmospheric pressure. On the other

hand, the peak intensity was not affected by the change of oxygen flow speed.

(2) Chemiluminescence method: Compound **1** is known to react with singlet oxygen in dichloromethane to form a stable dioxetane. This dioxetane reacts with tetrabutylammonium fluoride to give the singlet excited state of a lactone **2** which emits light at 456 nm.



1 **2**

This chemiluminescence reaction was applied for the determination of singlet oxygen generated from the generator. A gas stream from the dye sensitizer probe was bubbled through a dichloromethane solution of **1** placed in the receiver at 0°C and the solution was treated by the same way to give chemi-luminescence at 456 nm (Fig. 3), further proving the generation of of singlet oxygen.

This method can be used for the semiquantitative estimation of the actual amount of singlet oxygen produced from the generator. We estimated that the yield of singlet oxygen is at least 3 % at 30 ml / min of oxygen flow speed.

CONCLUSION —— We succeeded to construct a generator producing singlet oxygen in gas phase. The generator will be useful not only for the experimental studies on the behaviors of singlet oxygen to biological and memedical systems, but also for environmental research such as the degradation of hazard substances.

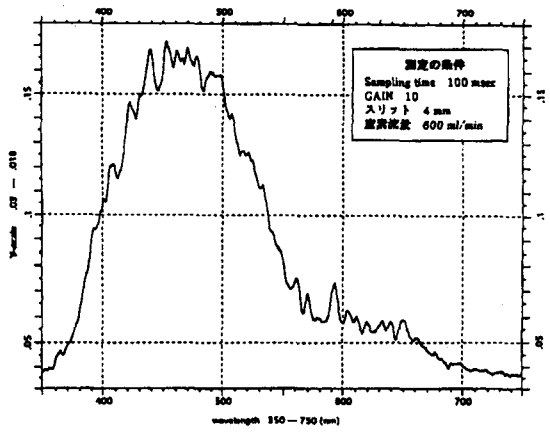


Fig. 3. Luminescence spectrum obtained from the reaction of compound 1 with singlet oxygen.

Acknowledgement —— The authors thank all of the co-workers who have made invaluable contributions to this research and also thank Professor Seiichi Matsugo and his co-workers for their efforts on searching dye sensitizer probe materials.

REFERENCES

1. For recent topics, see Symposium-in-Print on Singlet Oxygen (1999), *Photochemistry and Photobiology* 70, 476-548.

2. Frimer, A. A., Editor (1985–) Singlet Oxygen, Vol. 1–4, CRC Press, Boca Ranton. Wasserman, H. H. and R. W. Murray (1979) Singlet Oxygen, Academic Press, New York.

3. I. Mizumoto, S. Mashiko and N. Suzuki (1991) Charge integrating amplifier in the near-infrared region using an In GaAs PIN photodiode. Appl. Spectr., 47, 1462-1463.