Blue-Laser Enhancer-Free Singlet Oxygen Generation in Water and Heavy Water

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Abstract: We detect the generation of enhancer-free singlet oxygen in distilled water and heavy water upon illumination with a 405-nm laser radiation by measuring the quenching of the uric acid spectral peak at 294 nm.

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1. Introduction

Bregnhøj and Ogilby have recently reported the generation of singlet oxygen ($^1O_2$) without the use of photosensitizers in pure water and other solvents upon illumination by laser light [1]. They claim that the effect is due to two-photon excitation of an oxygen-solvent charge-transfer state (CT). Relaxation from the CT state yields excitation of the $^1O_2$ state [2]. They measure the phosphorescence of aerated samples in the 1275 nm region, which indicates the presence of a $^1\Delta_g$ upon excitation by 400-nm femtosecond (fs) pulses. The phosphorescence measurement required the implementation of photon counting techniques using near-infrared high sensitivity photomultiplier. There is a simple alternative way of detection of a $^1\Delta_g$ by the monitoring of the quenching of the UV peak of uric acid at 294 nm [3-5]. Uric acid dissolved in the samples reacts with the excited oxygen according to the Uricase reaction, which leads to the fading of the peak. The amplitude of the peak reduction measures the amount of $^1O_2$ present in the solvent.

In this work, we use the uric acid method to detect enhancer-free $^1O_2$ in pure distilled water and heavy water by using a continuous wave (CW) diode laser at 405 nm and fs-pulses excitation. The solution of uric acid at concentration smaller than one μM exhibits a clear quenching of its UV peak at 294 nm upon light treatment for several hours. The results confirm the previous findings reported about the inactivation of viruses without the use of photosensitizers [6].

2. Method

The experimental set-ups have been described elsewhere [6]. We conduct irradiation using the light from a pump laser (3-W CW diode laser at 405 nm and 200-mW doubled harmonic at 405 nm 140-fs light pulse from a Ti-Sapphire laser), which propagates toward the sample without using focusing optics. A magnetic stirrer mixes the sample to make sure the radiation affects all the volume. We avoid direct hitting of the light with the stirrers. The procedure continues for four to five hours. We measure the UV spectra in the 190-400 nm region using a UV-VI spectrophotometer (Evolution 201, Thermo-Scientific). We measure the spectra after each hour of irradiation.

The samples are double distilled water and deuterium oxide at 99.9% purity (Aldrich Chemistry). We prepare 0.5 μM solutions of uric acid in each solvent. We use a 1-cm pathlength quartz spectroscopic cell. We measure the concentration of dissolved oxygen in each sample using an optical detector (Vernier Optical Dissolved Oxygen Sensor). We study no aerated and aerated samples. We perform the aeration procedure by pumping air at normal conditions for several hours.

3. Results and Analysis

Figure 1a shows the UV spectrum of a solution of uric acid in water for a non-irradiated sample, and for after 2 hours irradiation and 5 hours irradiation, as indicated. For the irradiation, we use 3W of the CW diode laser light at 405 nm. The sample was previously aerated for five hours. We measure a concentration of oxygen of 10 mg/L before the start of the irradiation. The quenching of the uric acid peak at 294 nm becomes evident over time. We notice that a non-aerated sample exhibits much less quenching effect. Figure 1b shows similar results obtained for a uric acid solution in heavy water. For heavy water, we measure an oxygen concentration of 12 mg/L. We perform similar experiments using the 200-mW double harmonic from the Ti-Sapphire fs-laser at 405 nm obtaining equivalent results.

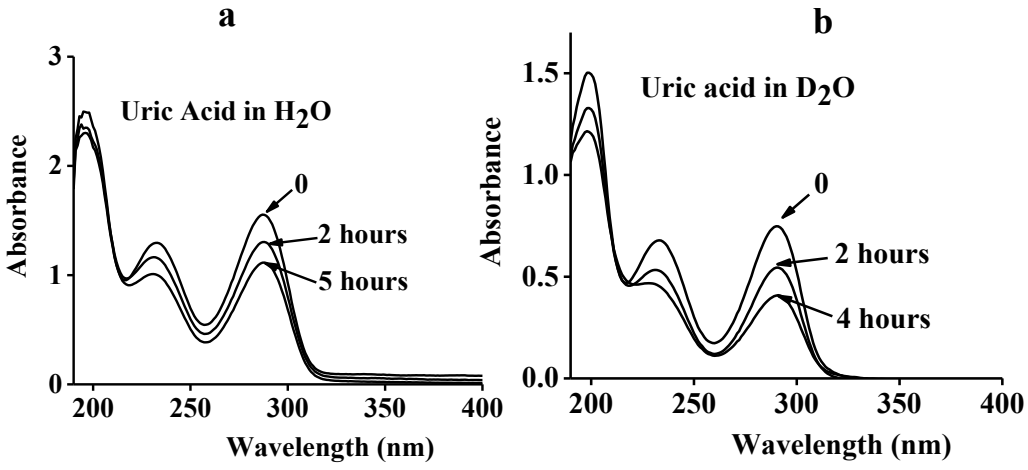

Figure 1. a) UV spectrum of uric acid in distilled water for different irradiation procedures as indicated; b) UV spectrum of uric acid in heavy water for different irradiation procedures as indicated.

4. Conclusions

We demonstrate that the use of the uric acid sensor confirms the generation of $^1O_2$ in pure water and heavy water without the presence of photosensitizers upon irradiation with blue laser light. The results validate the recent findings of Bregnhøj and Ogilby, who completed a more elaborate and complicated phosphorescence detection of $^1O_2$. The results have important implications for the generation of $^1O_2$ in natural waters only by the effect of light without the intervention of chemical enhancers and potential applications in photodynamic therapies.

5. Acknowledgments

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6. References

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