

## Electronic Supporting Information

### Photosensitisation Studies of Silicone Polymer Doped with Methylene Blue and Nanogold for Antimicrobial Applications

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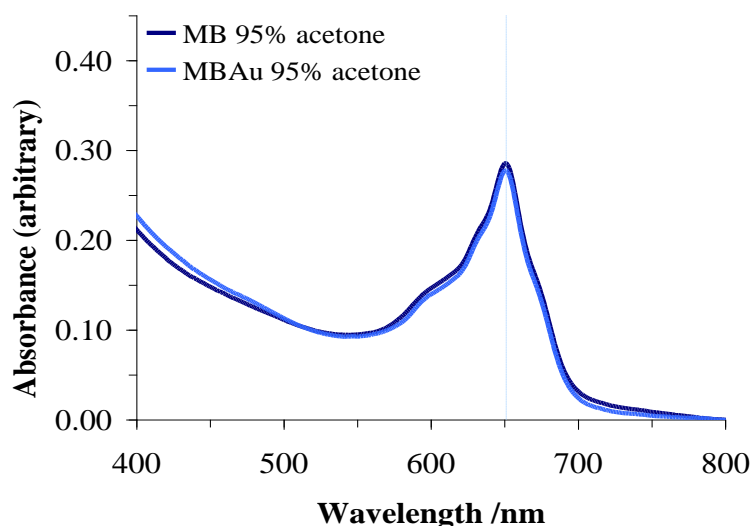
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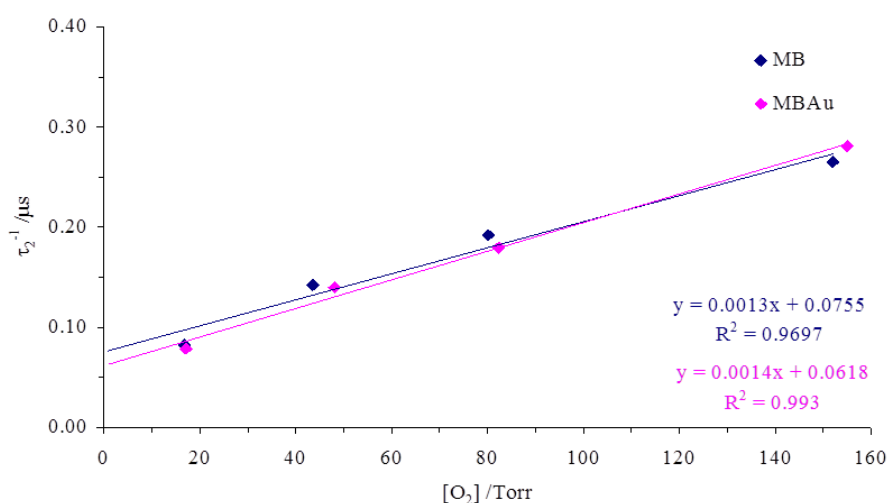
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A PerkinElmer Lambda 25 UV-Vis Spectrometer was used to measure the UV-Vis absorption spectra of MB- and MB + 2 nm gold nanoparticles (MBAu)- encapsulated in silicone catheter polymers between 400 - 800 nm. The sections were swelled in the presence of MB in a 95 % acetone swelling solution, with and without nanogold present, for 24 h under dark conditions as determined previously by [1]. Spectra were obtained at a scanning speed of  $480 \text{ nm min}^{-1}$  recorded through UV Winlab software® and an absorption maxima was determined at  $\lambda = 651 \text{ nm}$  (MB). The catheter segments were flattened to minimise optical distortion, although light scattering artefacts contribute to the apparent absorption below 500 nm.



**Fig. S1.** UV-Vis spectrum of MB- and MBAu- encapsulated silicone catheter sections prepared using a “swell-encapsulation-shrink” method. The sections were swelled in the presence of MB in a 95 % acetone swelling solution, with (MBAu) and without (MB) nanogold present, for 24 h. Absorption peak maximum:  $\lambda = 651 \text{ nm}$

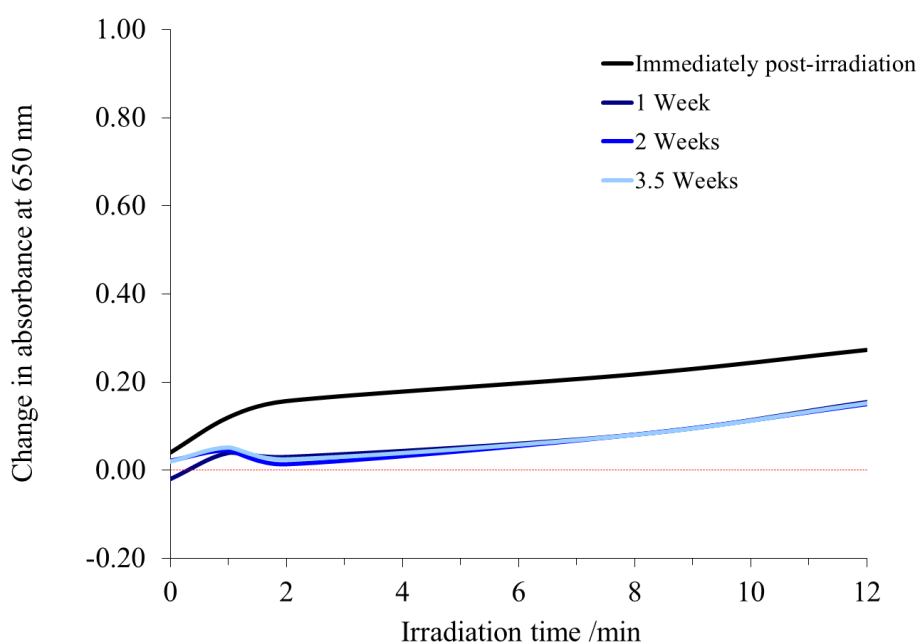


**Fig. S2.** Stern-Volmer analysis of time-resolved singlet oxygen emission when MB is encapsulated in a silicone catheter matrix, with (MBAu) and without (MB) the presence of 2 nm Au nanoparticles. The inverse of the rise-time lifetime is plotted vs. oxygen levels, according to equation 2 (main text).

The Stern-Volmer plot (see Eq 2, main text) demonstrates the inverse linear dependence of the photogeneration lifetime of singlet oxygen (which we assume is equivalent to the triplet state lifetime) vs. oxygen partial pressure when MB is encapsulated in the silicone catheter matrix, with and without the presence of 2 nm Au nanoparticles (Fig S2). Using an estimate of the interpolated intercept (0.07) by assuming linearity, we can estimate the lifetime of the triplet state in the matrix under deoxygenated conditions as c. 14  $\mu\text{s}$  ( $k_d^T$ ) which is considerably smaller than the value measured in deoxygenated aqueous solution (80  $\mu\text{s}$ ) [2]. Thus using this analysis we infer that some quenching of the MB triplet state must occur in the silicone matrix.

The MB triplet state lifetime in air-equilibrated aqueous solution is 1.8  $\mu\text{s}$  [2], whereas the lifetimes observed in the air-exposed polymer are c. 3-4  $\mu\text{s}$ . The rate constant for quenching is presumably limited by the rate of oxygen diffusion within the matrix which will be lower than for aqueous solution. On the other hand oxygen solubility in the polymer is probably higher than for aqueous solution at the same partial pressure by analogy with the higher solubility of oxygen in organic solvents.

The photostability of the MBAu-encapsulated silicone catheter polymer was investigated. Sections of the MBAu-encapsulated silicone catheter polymer were immersed in 250 mL PBS and irradiated with red laser light (660 nm, 230 mW, Periowave, Ondine Biopharma Inc.) using a microlens fibre for increasing time periods, up to 12 mins. The UV/vis spectral absorption of the samples, both prior to and post irradiation, was analysed at 650 nm (Dynamex MRX TCII). The samples were stored under dark, dry conditions and the absorbance at 650 nm was re-measured periodically to determine whether the initial photodegradation of the polymer was reversible.

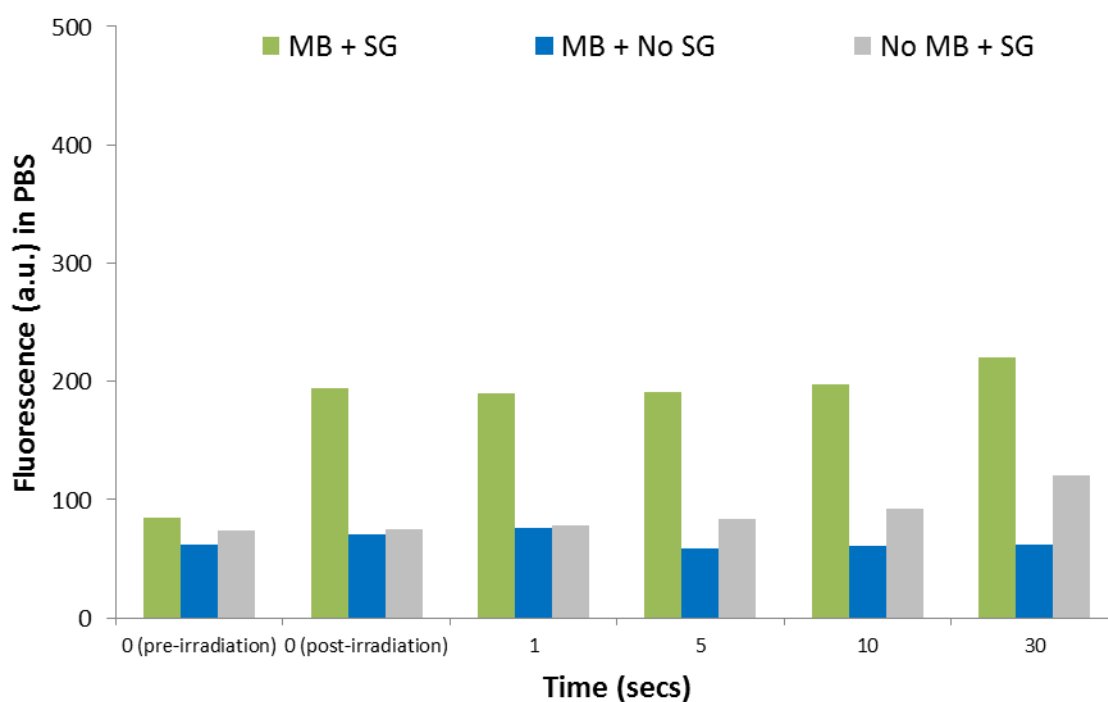


**Fig. S3.** The change in absorbance at 650 nm of the MBAu-encapsulated catheter sections exposed to laser irradiation (660 nm) for increasing periods of time, immediately post-irradiation and after extended periods under dark conditions.

The photostability of the MBAu-encapsulated silicone catheter was investigated through changes in absorbance intensity at 650 nm upon increasing 660 nm laser irradiation time (min) to establish photobleaching effects of MBAu-encapsulated silicone catheter sections. Immediately following

irradiation, a noticeable increase in absorbance was detected at 650 nm, indicative of photobleaching effects. Moreover, short-term storage under dark, dry conditions effected a slight, yet limited recovery of photobleaching effects, demonstrated by a decrease in the change from the initial absorbance (pre- laser irradiation).

The indirect detection of singlet oxygen ( $^1O_2$ ) was measured, prior to and following laser light irradiation of polymer samples, through photo-induced green fluorescence emission of the Sensor Green (SG) reagent, diluted in PBS prepared using  $H_2O$ . Results demonstrated the production of  $^1O_2$  was doubled following irradiation of MBAu-encapsulated silicone polymer samples (MBAu + SG) in comparison to control groups, which either lacked photosensitive dye (no MBAu + SG) or the  $^1O_2$  detecting SG reagent (MBAu + no SG). However, the fluorescence detected in PBS was significantly less than that observed in deuterated solution, which is consistent with the literature as  $D_2O$  is known to extend the lifetime of singlet oxygen (Fig 7). Autofluorescence was detected prior to light irradiation (time 0) for all three samples.



**Fig. S4.** Indirect detection of singlet oxygen measured through green fluorescence emission ( $\lambda_{ex/em}$  480/530 nm) using 1  $\mu$ M Sensor Green (SG) reagent in phosphate buffered saline (PBS). Fluorescence measurements were taken at 0 sec before (pre-irradiation) and 0-30 secs after (post-irradiation) red laser light administration ( $45 J cm^{-2}$ ) to MBAu-encapsulated and control (no MBAu) silicone polymer flat sheet samples at 670 nm using a microlens fibre. Selected time intervals were chosen following the initial light irradiation for up to 30 mins.

## Reference List

- [1] S. Noimark, C.W. Dunnill, C.W.M. Kay, S. Perni, P. Prokopovich, S. Ismail, M. Wilson, and I.P. Parkin, The incorporation of methylene blue and nanogold into polyvinyl chloride: a new approach for light-activated disinfection of surfaces, *Journal of materials chemistry*, 22 (2012) 15388-15396.
- [2] M. Gonzalez-Bejar, P. Montes-Navajas, H. Garcia, and J.C. Scaiano, Methylene blue encapsulation in cucurbit[7]uril: laser flash photolysis and near-IR luminescence studies of the interaction with oxygen, *Langmuir*, 25 (2009) 10490-10494.