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Plasmon Enhanced Degradation of Organic Dye Pollutant through Reactive Oxygen Species Generation by Gold Nanorods

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Abstract

Gold nanorods (AuNR) upon ultrafast resonant irradiation are known to generate pressure shockwaves and reactive oxygen species (ROS) that are useful for biomedical applications, such as virus and pathogen inactivation and drug delivery. While using rhodamine B as a fluorescence probe to study excitation dynamics of AuNRs, we found an unusual degradation of rhodamine B. We present evidence that this degradation is mediated by the generation of ROS and use this effect to investigate the impact of nanorod morphology and laser intensity on the generation of ROS. We monitored solutions of a few micromolar rhodamine B and AuNRs in 1cm pathlength quartz cuvettes, temperature controlled within ±2 K, and magnetically stirred. These solutions were repeatedly exposed to 800nm 100fs ultrafast laser pulses. Subsequently, the fluorescence was measured by excitation with a 528nm continuous wave (CW) laser. We further confirmed the decreased concentration of rhodamine B by comparing the absorbance spectra of samples before and after exposure. We found an exponential decay in the fluorescence of rhodamine B associated with repeated irradiation of nanorods suggestive of first order kinetics. We also found a non-linear relationship of the rate of degradation with the ultrafast laser intensity. These findings lay the groundwork for better experimental techniques in detection of ROS generated by AuNRs and potentially aid in degradation of rhodamine B, which is an environmental pollutant in water systems.

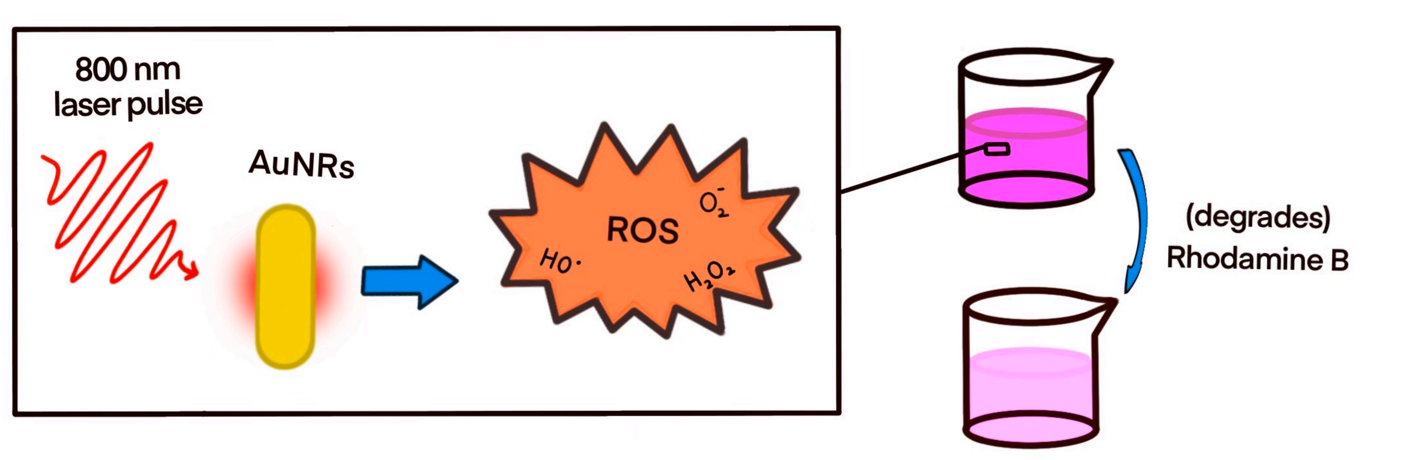

Figure 1. Graphical representation of ROS generation, which we hypothesize degrades rhodamine B.

What is Rhodamine B?

- A bright red-violet synthetic dye
- Popular temperature dependent fluorescent probe
- Widely used as textile and paper dye, and pigment for paint
- Has become a water pollutant due to poor disposal of wastewater from above industries
- Poses environmental and biological risks (known to induce skin/eye irritation and is toxic to fish)

Reactive Oxygen Species

- Highly reactive chemicals formed from diatomic oxygen (O_2)
- Involved in many biological processes such as cell signaling and homeostasis, but harmful if overproduced, causing cancer and damage to DNA

Objectives

- Confirm rhodamine B degradation by reactive oxygen species (ROS) generation by gold nanorods
- Investigate impact of laser intensity on rhodamine B degradation and ROS generation

Methods

Fluorescence spectroscopy
- Uses a beam of light to excite the electrons in molecules of certain compounds, which causes them to emit light, which is directed towards a filter and onto a detector for measurement of molecular changes

UV-vis spectroscopy
- Measures the amount of transmitted or absorbed light across the ultra-violet to visible light spectrum
- The absorbance spectrum can be used to analyze concentration levels in samples

Setup:

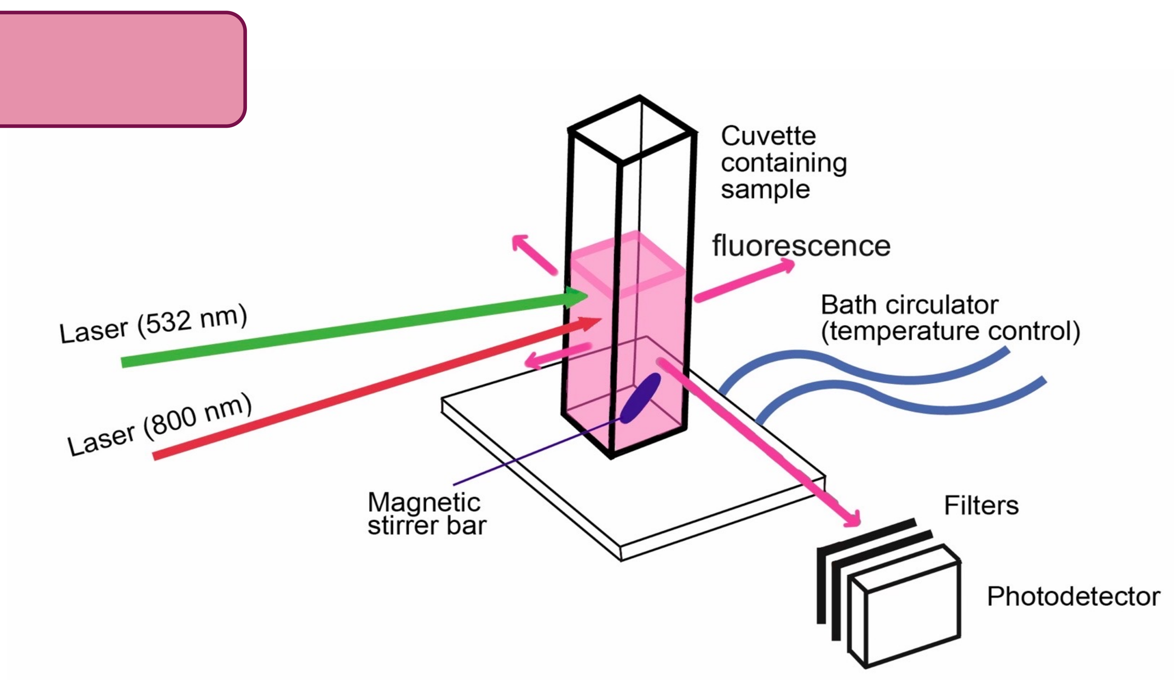

Figure 2. A setup of rhodamine B and AuNR solution in a quartz cuvette, exposed to 800 nm laser and 532 nm laser, with a photodetector and filters positioned at 90 degrees to the laser beams to collect fluorescence.

Results

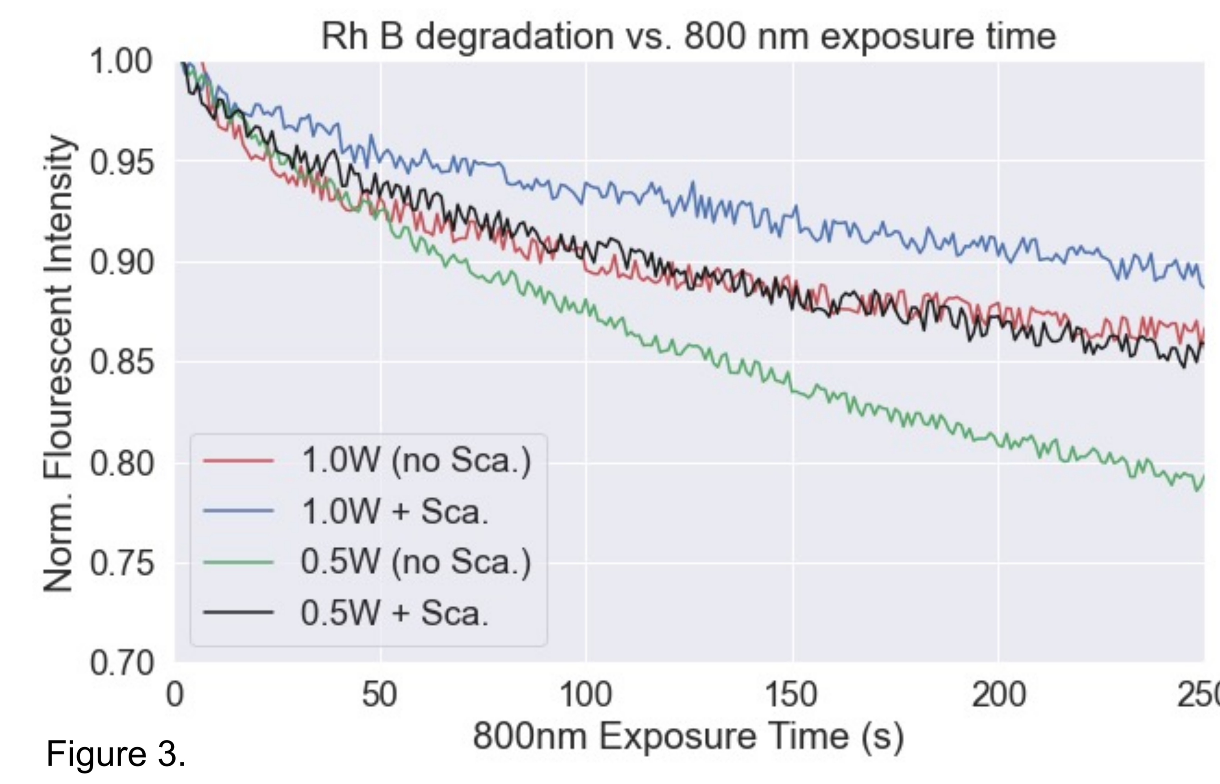

Figure 3.

Fluorescence intensity over time reveals a faster rate of decrease with solutions of rhodamine B and gold nanorods versus solutions of rhodamine B and gold nanorods with reactive oxygen species scavengers. Figure 3 also shows a faster decrease for solutions exposed to higher laser power of 1 Watt vs .5 Watts.

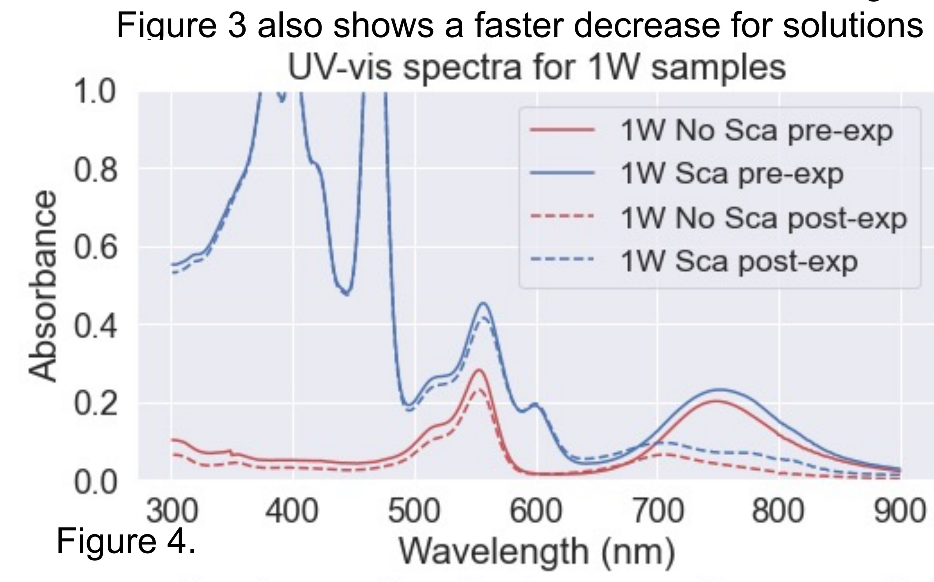

Figure 4.

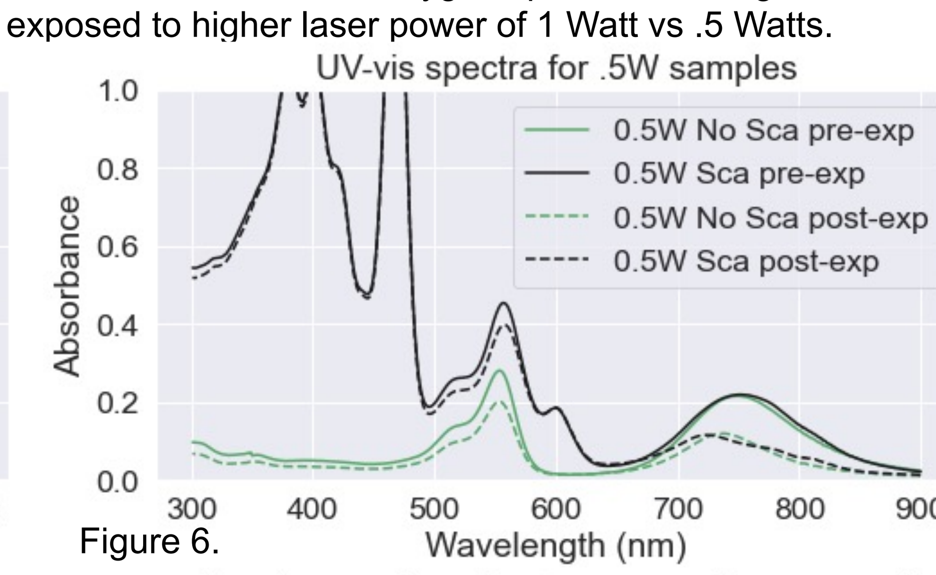

Figure 6.

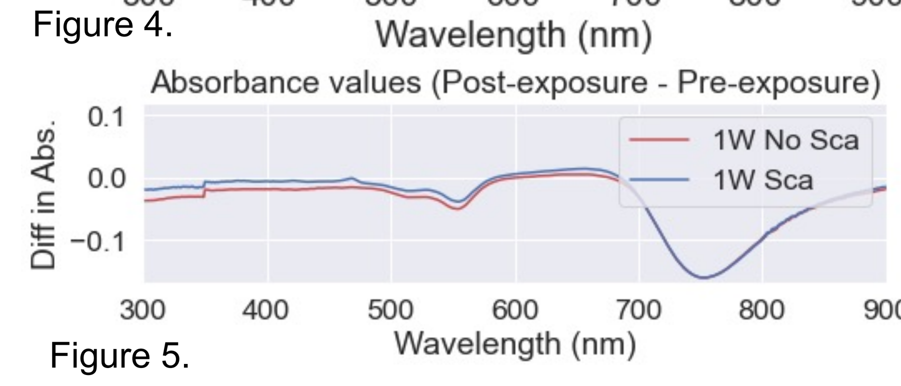

Figure 5.

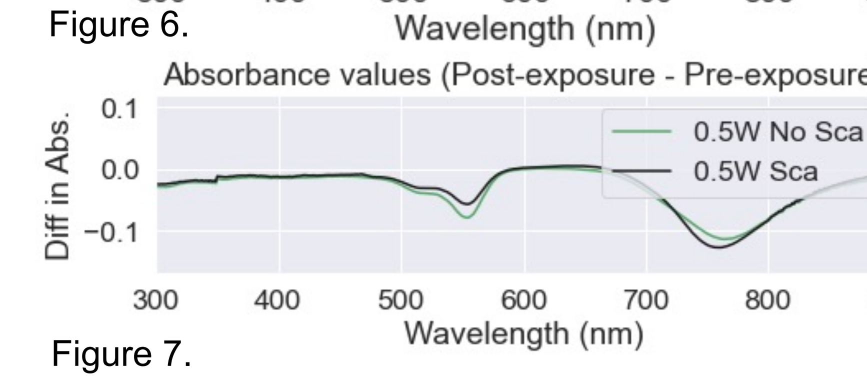

Figure 7.

- Rhodamine B absorbance spectra peaks around 550 nm (figure 4 and 6)
- Gold nanorods peak around 750 nm (figure 4 and 6)
- Comparisons of the spectra before and after exposure to the 800 nm laser (Figure 4 and 6) confirm a greater decrease in rhodamine B for samples without ROS scavengers, this difference can also be seen in the dip of Figure 5 and 7 that graphs the difference between post-exposure and pre-exposure spectra.

Conclusions

- Partially supports the hypothesis that the degradation of rhodamine B is caused by reactive oxygen species generation by gold nanorods
- Exponential decay in the fluorescence of rhodamine B associated with repeated irradiation of nanorods suggestive of first order kinetics
- Found a non-linear relationship of the rate of degradation with the 800 nm laser intensity

Future work

- Prepares for better experimental techniques in detection of ROS generated by AuNRs
- Aim to get more data for different nanorod morphology

References

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Acknowledgements

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