Measuring Kinetics Of Hydroxyl Radical Production By Photoactive Titanium Dioxide Nanoparticles In Natural Systems

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Introduction

Although nanoparticle use dates back to the nineteenth century, relatively little is known about their environmental impact. Titanium dioxide (TiO_2) nanoparticles possess unique ultraviolet light (UV) absorbing capabilities and photoactive properites. These characteristics give TiO_2 nanoparticles several useful industry applications including its use in food, pharmaceuticals, cosmetics, and protective coatings. This widespread use of TiO_2 makes the environmental risks it poses a great concern because of its ability to generate potentially toxic reactive oxygen species (ROS) after UV exposure. Hydroxyl radicals (OH·) are the most reactive type of ROS, making their rate of production particularly important. Quantifying this rate, mediated by different morphologies of TiO_2, is an important step toward acquiring knowledge of TiO_2's photoactive capabilities in environmental media.

Methods

Experiments simulated different morphologies of TiO_2 nanoparticles in a natural environment during sunlight exposure. Coumarin concentration was used to measure the relative rate of OH· production due to its reactivity to OH· and unique maximum light absorption at 280nm. Three morphologies of TiO_2 nanoparticles were tested: P25, TM3, and TM4.

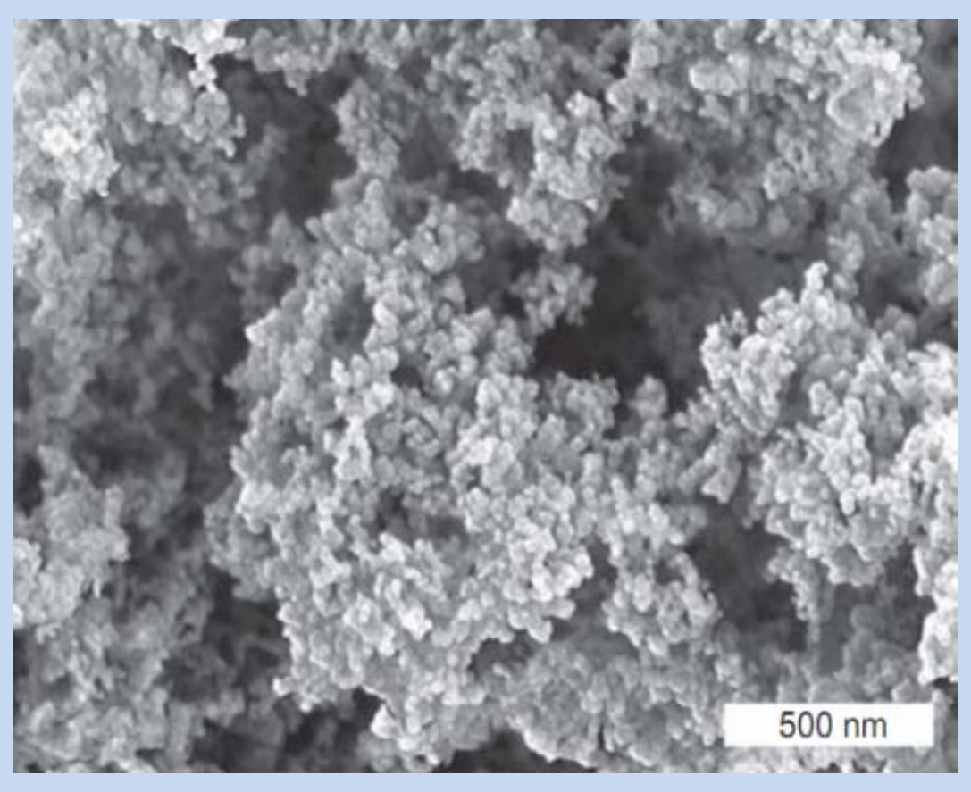

Fig. 1. SEM of TiO_2 P25

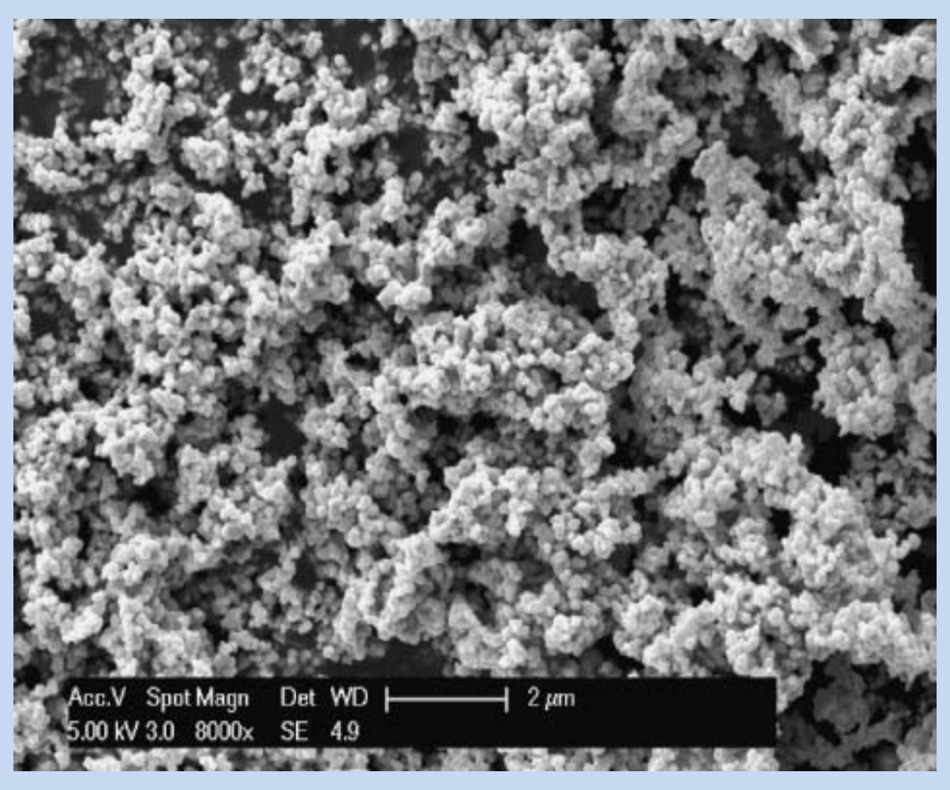

Fig. 2. SEM of TiO_2 TM3

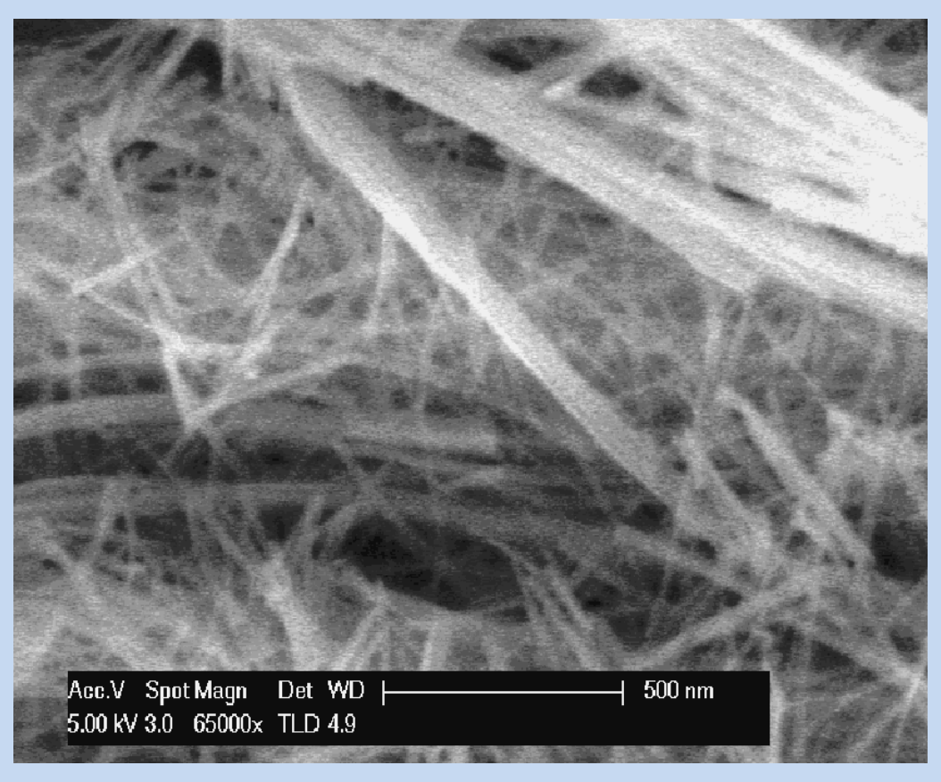

Fig. 3. SEM of TiO_2 TM4

- $10 mgL^{-1}$ of TiO_2 samples were used per trial
- 10^{-4} M coumarin was used per trial
- Magnetic stirring was used to simulate natural water movement
- A UV lamp at 60A was used to simulate sunlight
- Samples of solution were taken at 15 minute intervals

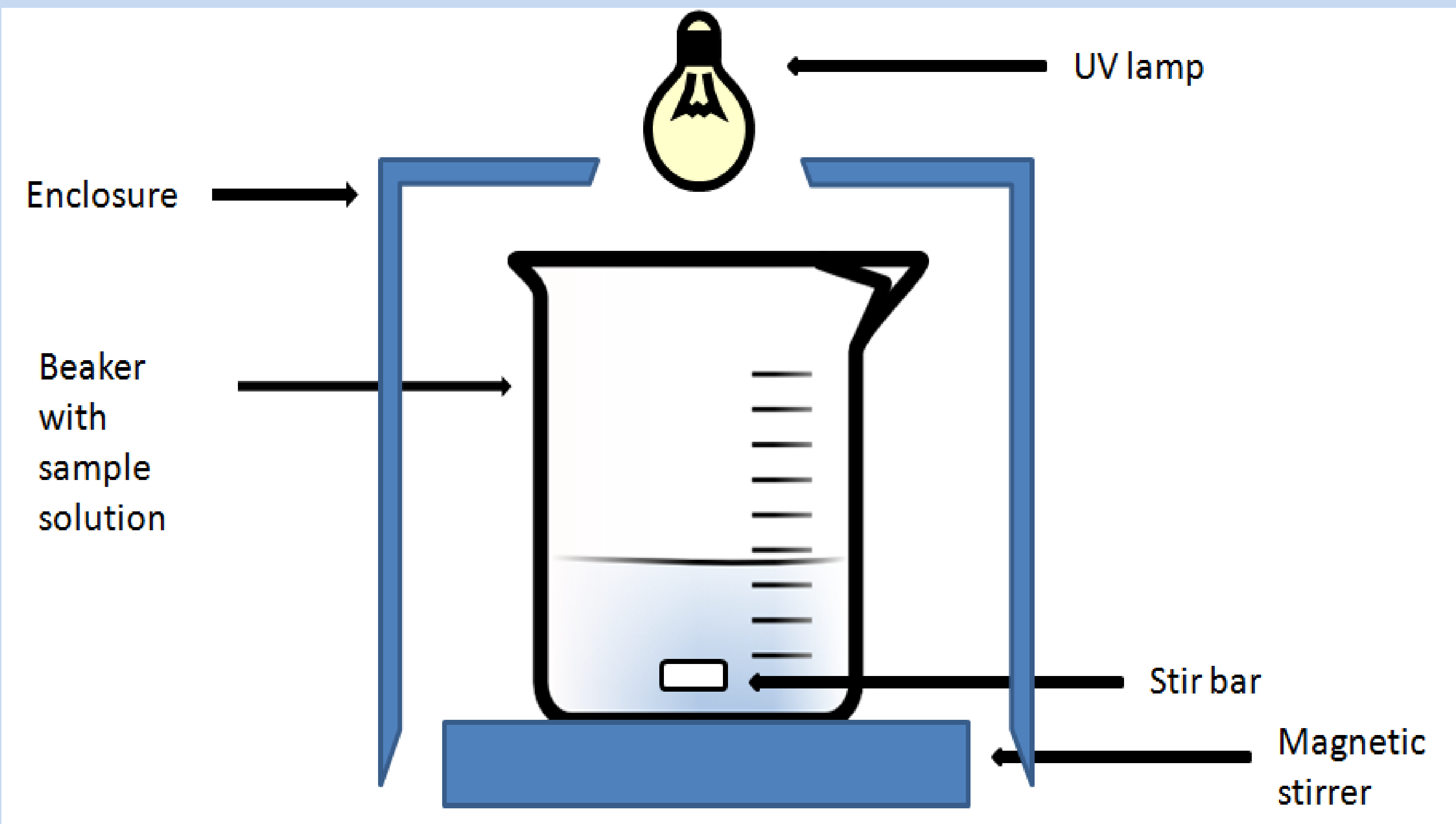

Fig. 4. Experimental setup

Results

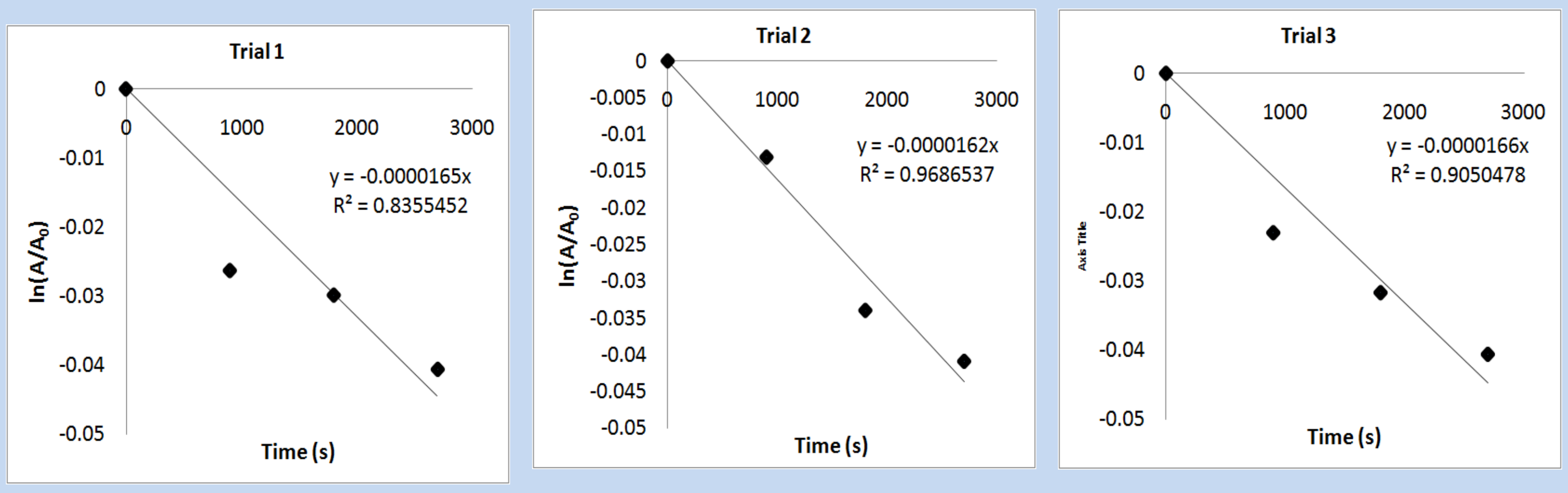

Fig. 5. Calculated rate constants forTiO$_2$ P25

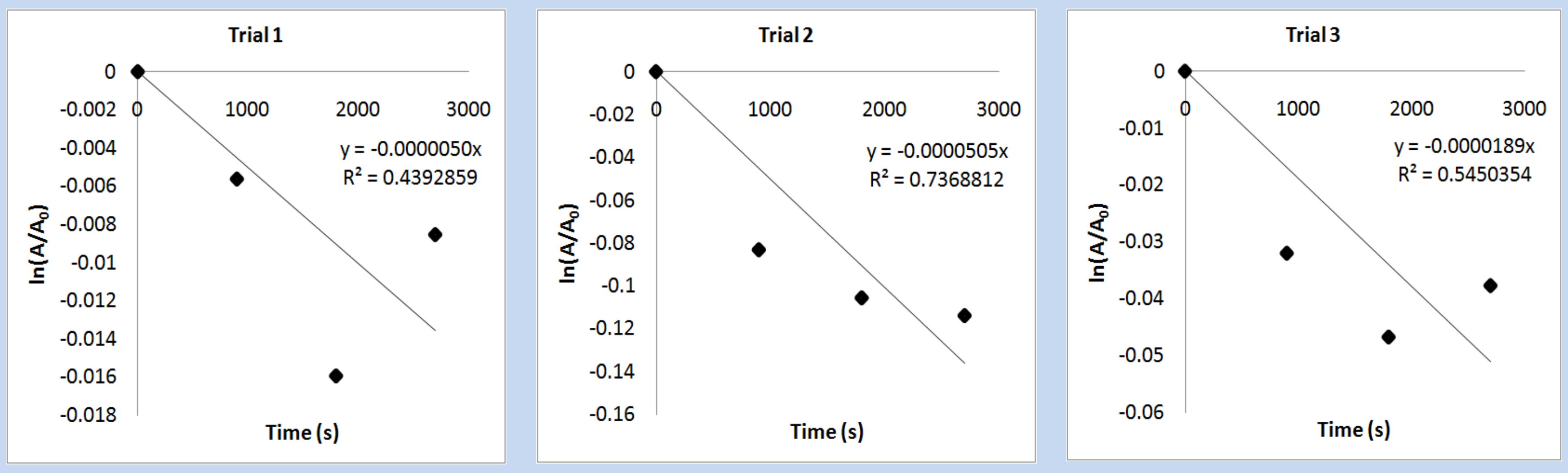

Fig. 6. Calculated rate constants forTiO$_2$ TM3

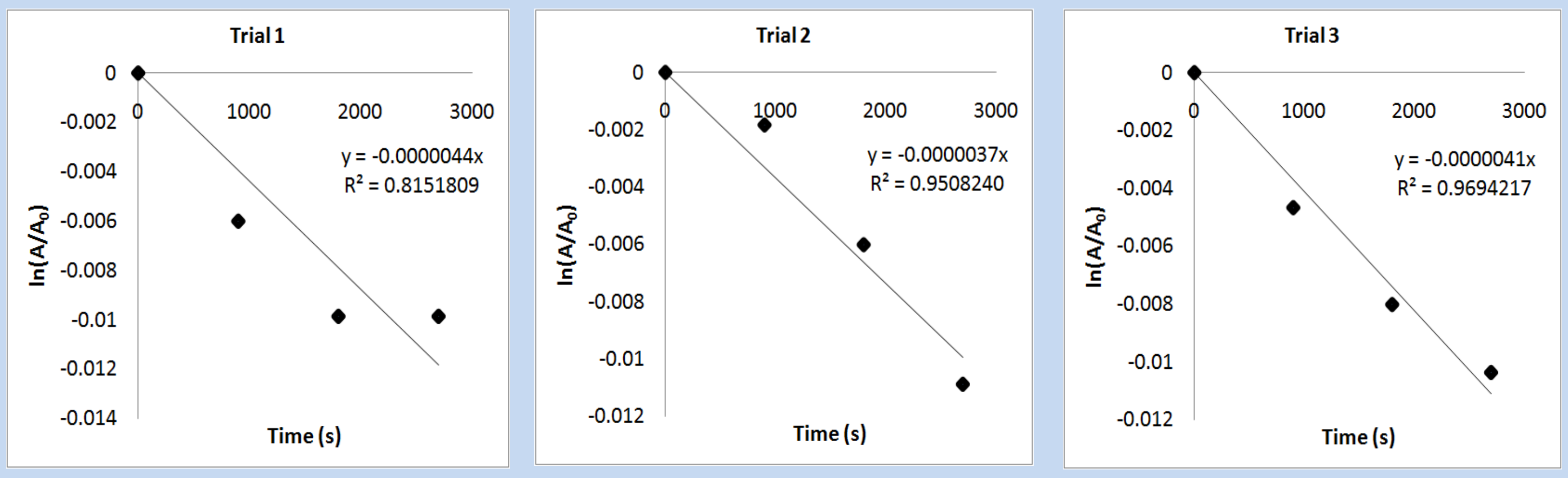

Fig. 7. Calculated rate constants forTiO$_2$ TM4

Summary

TiO_2 Concentration & Morphology	Average Rate Constant	Error
$10\ mg^{-1}$ TiO_2 P25	$1.643 \times 10^{-5}\ s^{-1}$	1.202×10^{-7} (0.73%)
$10\ mg^{-1}$ TiO_2 TM3	$2.48 \times 10^{-5}\ s^{-1}$	1.35×10^{-5} (54.44%)
$10\ mg^{-1}$ TiO_2 TM4	$4.07 \times 10^{-6}\ s^{-1}$	2.03×10^{-7} (4.99%)

Conclusion

Preliminary results indicate that TM3 has the highest rate of OH· production at $2.48 \times 10^{-6}\ s^{-1}$, although the rate also possesses the highest margin of error at 1.35×10^{-5}. P25 has a rate approximately four times that of TM4, $1.643 \times 10^{-5}\ s^{-1}$ and $4.07 \times 10^{-6}\ s^{-1}$, respectively. Both have relatively small margins of error at 1.202×10^{-7} and 2.03×10^{-7}, respectively. Alternative kinetics experiments must be conducted to verify the results.

Acknowledgments

National Science Foundation

California NanoSystems Institute