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PHOTOCATALYTIC CHARACTERIZATION OF FLUORINATED METAL PHTHALOCYANINE/METAL OXIDE HYBRID MATERIAL DEGRADATION BY REACTIVE OXYGEN SPECIES

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14. ABSTRACT

Experimentation with fluorinated metal phthalocyanine and metal oxide nanoparticles (Titania) shows the formation of a hybrid compound with increased production of reactive oxygen species (ROS) as well as resistance to ROS attack in aqueous solutions. The ultraviolet-visible spectrophotometer analysis of methyl orange degradation by the hybrid has shown 90% of methyl orange was degraded by 10 hr while the Titania alone has only degraded 24%.

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INTRODUCTION

Metal pthalocyanines have been known to show catalytic properties stemming from their 18π electron system; one such application of interest is the oxygen reduction potential. Specific metal phthalocyanines are photoactive and can generate singlet oxygen molecules by white light irradiation; however, in aqueous solutions, typical carbon-hydrogen bonded phthalocyanines are susceptible to attack from the singlet oxygen.

Discovery of novel fluorinated metal pthalocyanines (FxPcM) compounds has given the opportunity to explore potential photocatalytic reactive oxygen species (ROS) generating systems without catalyst degradation. Due to the highly hydrophobic nature of FxPcM, it can be expected that difficulties with aggregation in aqueous solutions will arise. This work has created a hybrid catalyst suspension in aqueous solution that will not only generate ROS but will also have long term viability and stability. Figure 1 shows the general formula of FxPcM.

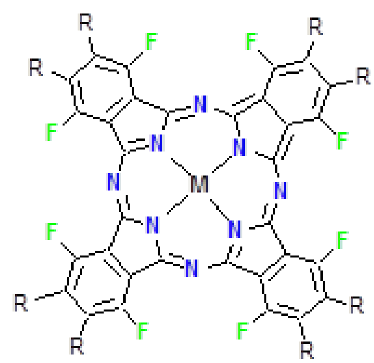


Figure 1
A general formula of FxPcM

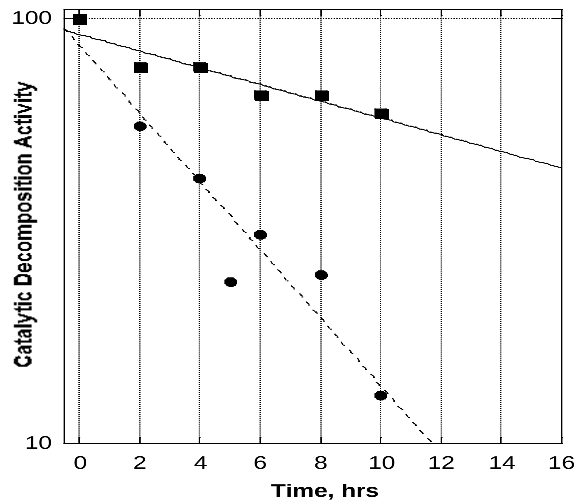
The hybrid material has the FxPcM on a metal oxide (MxOy) support. The metal oxide, Titania for example, has some inherent ROS generation properties, and it should be expected that the performance of the hybrid would be significantly higher. The performance of the FxPcM/MxOy hybrid and the MxOy alone will be quantified by the degradation of the singlet oxygen trap methyl orange dye.

EXPERIMENTAL

The organic metal oxide complex was synthesized by a microwave reactor. Approximately 1.0 g of the hybrid material was suspended by addition in 50.0 mL of aqueous methyl orange solution. The suspended material was simultaneously irradiated with white light and fed atmospheric air. Aliquots of methyl orange solution was taken and analyzed hourly by ultraviolet-visible (UV-Vis) spectrophotometry. This procedure was repeated with approximately 1.0 g of metal oxide to observe the difference in performance. A qualitative analysis of the fluorinated metal phthalocyanine alone was performed to determine whether it contributed any effect individually.

DISCUSSION

The rate of methyl orange dye degradation by the hybrid composite material, seen in figure 2, has been observed to be significantly more effective than the metal oxide alone. By the tenth hour of white light irradiation, almost 90% of the methyl orange had been degraded by the hybrid material.



Note: Squares represent the solely solid-state support material - TiO2, and circles represent the F64PcZn organic material on the TiO2 solid-state support hybrid.

Figure 2
Time dependent concentration decrease in methyl orange dye represented on a log scale 10 to 100

Since testing with the fluorinated phthalocyanine alone showed no degradation, the synthesized hybrid material shows characteristics of an entirely new complex. During the UV-Vis spectrophotometric analysis, no phthalocyanine was observed in solution confirming that the organic component of the catalyst does not leech in aqueous solutions. This is the desired effect when fluorinated aliphatic chains were bonded prior to complex formation. The spectroscopic analysis after extracting the hybrid material with an organic solvent showed that the phthalocyanine structure had not been altered, confirming the viability of the catalyst during such reactions.

A visible decrease of the methyl orange dye can be seen in figure 3 as irradiation time increases. More importantly, as methyl orange is also a pH indicator, it is important to note that there has been no color change. The lack of color change suggests that the degradation process did not generate acids that would lower the pH.

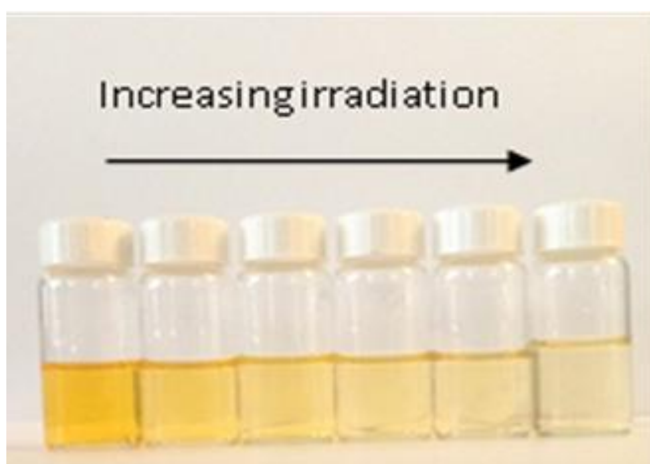


Figure 3
Six methyl orange dye solutions in order of shortest to longest irradiation duration

CONCLUSIONS

The hybrid composite consisting of a metal oxide and a fluorinated metal centered phthalocyanine shows improved catalytic rate of generating reactive oxygen species. In addition, the hybrid shows resistance to leeching in aqueous solutions without compromising performance. The development of the hybrid material is in its infancy, and further research is being developed to explore its capabilities.

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