

Isolating the Photocatalytic Degradation of Methylene Blue Dye on TiO₂ Surface

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Photocatalytic degradation of organic molecules has a broad applicability and has been studied with particular intensity for the purpose of water and air purification [1]. In this process, light is absorbed by a semiconducting material and converted to electron-hole pairs, which in turn react with water molecules to form hydroxyl radicals ($\bullet\text{OH}$). These highly oxidative molecules go on to degrade organic molecules through what is known as an Advanced Oxidation Process (AOP) [2]. However, the result is usually achieved through diverse pathways, and isolation of the individual mechanisms is difficult. In particular, this experiment is designed to isolate the degradation of an organic marker at the surface of the catalyst material, as opposed to degradation away from the catalyst surface (*i.e.* within the aqueous medium). This has been achieved by designing an experiment to observe the relative mass of methylene blue (MB) on the catalyst surface during a photodegradation reaction. The TiO₂ film was deposited onto glass beads in order to immobilize the catalyst material on a visibly transparent substrate, allowing measurement of dye concentration via visible light spectroscopy.

In preparation for this experiment a thin film of nanocrystalline TiO₂ was deposited onto the surface of borosilicate beads of 1 mm diameter. This was accomplished by mixing the glass beads into a solution of water, TiO₂ powder, polyacrylic acid, and tetraethylorthosilicate. The beads were then removed from the solution, tumble dried, and finally heat treated in open air at 600C for 8 hours. SEM micrographs of one bead from this batch are shown in Figure 1. Next the beads were mixed in a solution of water and MB for several minutes and then removed. It was determined that 12.8 mg of MB had adsorbed to the TiO₂ surface by measuring the concentration of MB in the water before and after the addition of the beads using a Shimadzu UV-3600 Spectrophotometer. In order to measure the relative amount of dye on the surface of the beads, the beads were packed into a quartz cuvette and the beads' absorption of visible light was measured and compared to a reference spectrum collected from the beads before they were soaked in the MB solution. The dyed beads were then packed into a small photoreactor and illuminated with light from a Newport solar spectrum simulator, model 69907, calibrated to AM 1.5 conditions as shown in Figure 2. After 2 min of illumination the relative absorbance was measured again. This process of illumination and measurement was then repeated two more times. The amount of remaining dye as a function of time was calculated from the relative height of the 572nm absorption peak above the reference. This data was plotted along with the raw data in Figure 3. This experiment presents a novel approach to for quantifying photocatalytic degradation on a catalyst surface: in this case the overall result was a degradation of 92% of the MB after 6 min of illumination. This result was 5 times faster

than a control experiment using the same process, but without the addition of catalytic beads to the reaction chamber.

References:

- [1] Lazar, M. A., Varghese, S. & Nair, S. S., *Catalysts* **2**, 572–601, 2012
 [2] R. Andrezzi, *et.al.*, *Catalysis Today*, vol. 53, no. 1, pp. 51–59, Oct. 1999.
 [3] The authors would like to thank the Research Experience for Undergraduates, Louis Stokes Alliances for Minority Participation, and Undergraduate Research Mentorship Program.

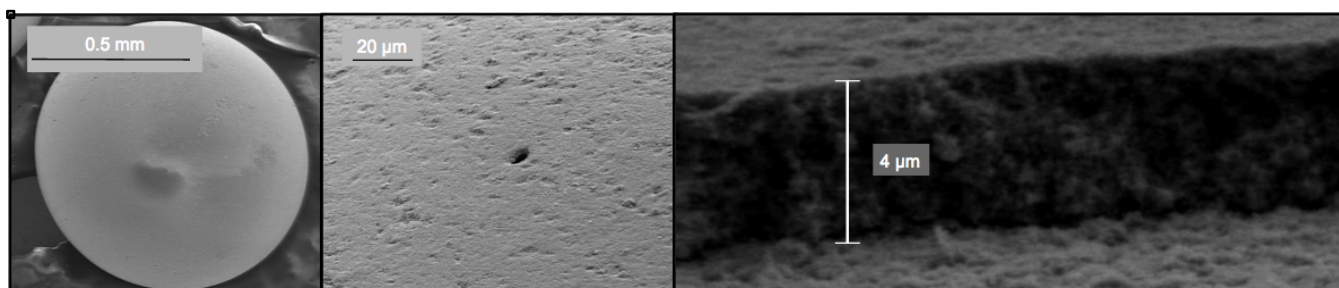


Figure 1. SEM micrographs of coated beads showing the uniformity and macrostructure of the coating. Removal of a small area of the coating with a razor reveals a 4 μm thickness of the TiO₂ layer.

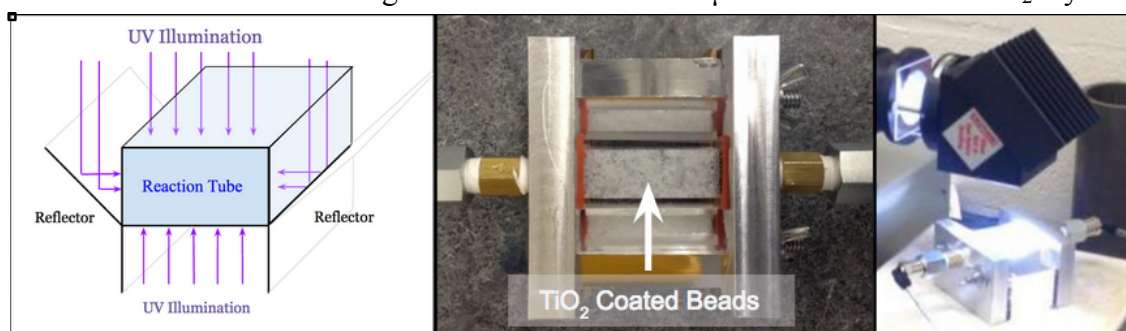


Figure 2. Photoreactor designed and used for these lab-scale tests of photodegradation reactions.

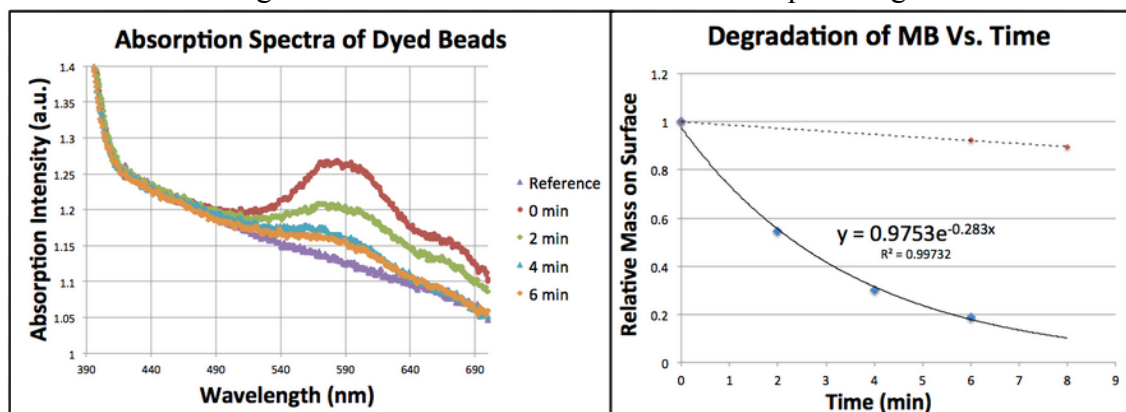


Figure 3. a) Raw data obtained from UV-vis spectroscopy of dyed beads; b) relative mass of MB on TiO₂ surface calculated from absorption spectra (control experiment plotted as dotted line).