

## Annealing Effects on TiO<sub>2</sub> Photocatalytic Degradation of Methylene Blue

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The degradation of organic molecules through semiconductor photocatalysis has been extensively studied, due to the process's potential as a solution for both energy and environmental problems, such as solar cell and water purification applications. During photocatalysis in water treatment, the semiconducting material absorbs light and generates electron-hole pairs, which react with water molecules to form hydroxyl radicals ( $\bullet\text{OH}$ ) that can rapidly degrade organic molecules at the surface of the photocatalyst [1]. There are multiple annealing effects to material photoreactivity, one being crystal phase ratio between anatase and rutile phases, which can be quantified through Raman spectroscopy [2-3]. This work is a crystal phase analysis on a modified TiO<sub>2</sub> thin film, and the evaluation of annealing effects on the thin films' reactivity with respect to the photodegradation of an organic marker. The performed testing method is an extension of this group's previous work. In order to isolate the contaminant degradation by the catalyst, the metric for degradation is the relative mass of the organic marker Methylene Blue (MB) directly at the surface of the catalyst, rather than degradation away from the catalyst surface (such as concentration in an aqueous medium) [4]. The TiO<sub>2</sub> film was affixed to quartz slides in order for the film and relative mass of MB to be observable on a visibly transparent substrate, via visible light spectroscopy.

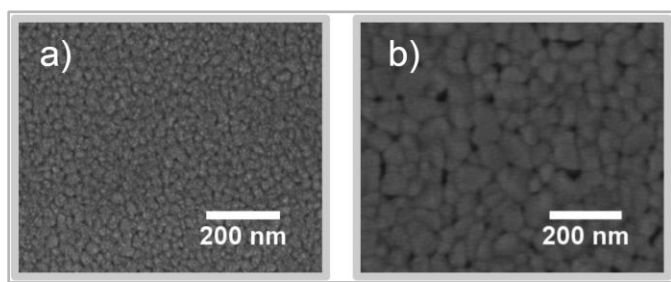
The sample preparation included a dip-coating process, using an ethanol-based sol gel of titanium tetraisopropoxide (20% solution) with 0.3wt% Degussa P25 and 0.05wt% SiO<sub>2</sub> nanoparticles suspended via pulse sonication. Quartz slides were cleaned and dipped into the sol gel twice at a rate of 6mm/s. This was followed by drying the slides at 150°C for one hour in open air. Next, the amorphous TiO<sub>2</sub>/P25/SiO<sub>2</sub> films were subjected to different annealing temperatures, at 600°C, 800°C, 900°C and 1000°C, in open air for two hours. An SEM micrograph of both the lowest and highest-temperature sample films are shown in Figure 1 (Zeiss Sigma VP FEG SEM). Raman spectroscopy was performed on each sample with a Horiba HR800-UV with a 532.2nm laser, and using a method from Castrejon-Sanchez, the phase ratio between anatase and rutile was calculated, shown in Figure 2 [3]. Next, the catalyst films were analyzed in a Shimadzu UV-3600 Spectrophotometer: Samples were spin-coated twice with 200 $\mu\text{L}$  of 0.1g/L MB solution, then incrementally exposed to 365nm light, as illustrated in Figure 3. The relative amount of MB was recorded by monitoring the absorption of MB at the 664nm peak and 610nm shoulder, followed by the deconvolution of Gaussian fit peak heights of each wavelength and time interval.

Degradation test results followed a pseudo-second order regime, which yielded degradation rates shown in Figure 4. The 600°C sample held the highest degradation rate constant. Meanwhile, both 900°C and 1000°C samples showed small to negligible degradation, with rate constants more than ten times smaller than the 600°C sample. SEM analysis shows that crystallites in the 1000°C film are larger, corresponding with rutile phase growth. This may explain the lowered degradation rate, as rutile phase TiO<sub>2</sub> has higher rates of electron-hole recombination, lowering catalytic activity. Larger crystallites also imply a lower film surface area, further inhibiting catalyst effectiveness. An interesting finding was the

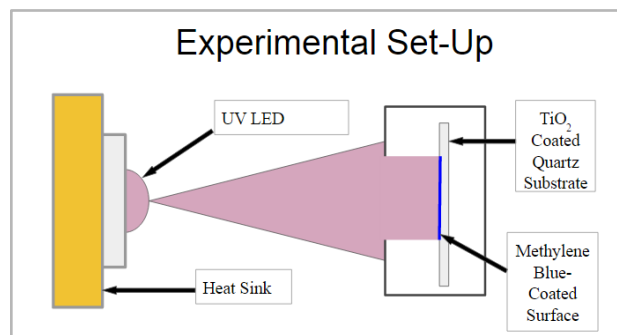
high temperature requirement for the modified TiO<sub>2</sub> to convert to rutile phase, with ~30% rutile occurring at a comparatively high temperature of 800°C. This could possibly be attributed to the sol gel synthesis method, the fused silica substrate, or the modifications in film precursors. This experiment demonstrates a modified approach to compare the annealing effects on a modified TiO<sub>2</sub> thin film to its propensity for photocatalytic degradation of an organic marker.

References:

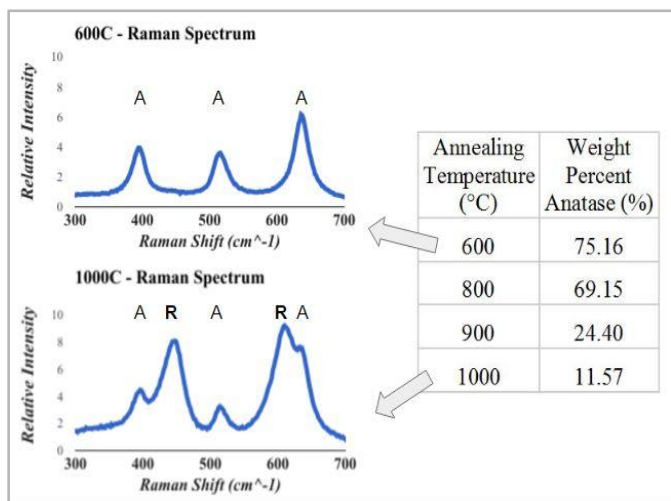
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 [5] This research is funded in part by the NSF/REU Site Program (grant No. 1560383), Portland State University Venture Development Fund, and Undergraduate Research Mentorship Program.



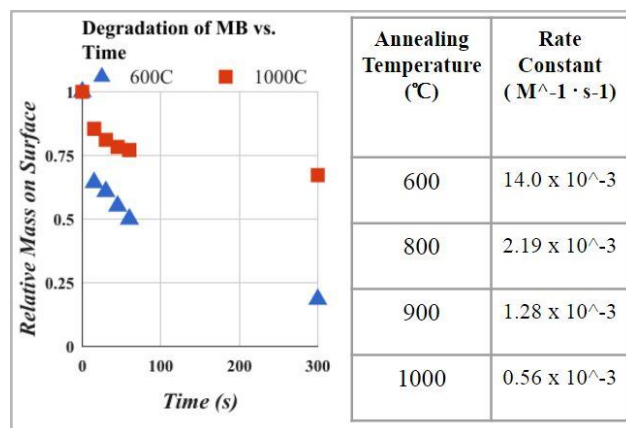
**Figure 1.** SEM micrographs of the modified TiO<sub>2</sub> films, at annealing temperatures of 600°C (a) and 1000°C (b).



**Figure 3.** Experimental setup for incremental MB degradation. LED used: LED Engin LZ1.



**Figure 2.** 600°C and 1000°C sample Raman spectra. Note the large rutile peak formations (R) in comparison to anatase (A). Table: sample calculated wt% anatase.



**Figure 4.** Relative mass of MB on 600°C and 1000°C TiO<sub>2</sub> films through degradation test. Table: corresponding rate constants for each sample degradation.