Effects of TiO_2 nanostructure and various ceramic supports in photocatalytic membranes for water treatment

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Introduction

The growing need for clean drinking water worldwide is one of the pressing issues of this century. The World Health Organization estimates that in 2005, 1.6 million children under the age of 5 died from causes due to unsafe drinking water.[1] Low-pressure membrane filtration systems are likely to play an important role in water purification and reuse strategies.[2] While these systems have low-cost and high-efficiency operation, chemical and biological fouling present challenges to this technology.

The goal of this work is to prevent membrane fouling by creating a novel reactive membrane filtration system that provides chemical and biological treatment of waters of degraded quality. By coating ceramic micro- and ultrafiltration membranes with highly active titanium dioxide photocatalysts, we aim to create membranes that degrade organic chemicals and inactivate microorganisms, thereby preventing flux decline and irreversible fouling.

Previous work in our lab has demonstrated that catalytic "hot spots" exist at the interface between the anatase and rutile phases of TiO_2[2]. With this in mind, we have set out to compare a variety of nanostructured materials of anatase and mixed phase catalysts prepared by reactive sputtering, sol gel synthesis, and other commercial methods. Additionally, we are investigating the effects of ceramic supports of different pore sizes and metal oxide materials to identify a highly active photocatalytic membrane filter.

Methods

Ceramic discs were obtained from Sterlitech Corporation. These discs have a layered structure, with a predominantly α-alumina base layer and a top layer to control pore size. Discs with a top layer pore size of 0.14 μm consisted of rutile titania particles, while discs with a top layer pore size of 300 KD (about 0.014 μm) consisted of zirconia particles. These discs were cleaned gently with acetone and with water and dried at 104 ºC before being coated with various active layers of TiO_2. Table 1 shows the set of active layers studied.

Table 1. Active Layers studied

Sputtered Anatase
Sputtered Anatase and Rutile Mixed Phase
Sol gel Anatase
Sol gel Anatase and Rutile Mixed Phase
Degussa P25

Magnetron Sputtering

Reactive dc magnetron sputtering was used to deposit anatase or mixed phase combinations of anatase and rutile particles (10-40 nm diameter) on the ceramic membrane discs. Pure titanium was used as the target and oxygen was the reactive gas. Phase composition of the active layer was selected by controlling sputtering power, RF bias, and angle of deposition, and was verified using grazing incidence diffractometry.[3]

Sol-gel Dip Coating

Nanoscale particles of anatase and mixed phase TiO_2 were made by the solvothermal method, through controlling the acidity of the sol.[4] A slurry of the nanoparticles (1.0 g/L) with sodium dioctyl sulfosuccinate (0.05 g/L) was stirred and then sonicated for 1 hour.[5] The top side of each disc was carefully dipped into the solution and withdrawn by hand. After each dip, the disc was dried at 104 ºC, and then heated with a ramp rate of 5 ºC per minute up to 450 ºC to dwell for 1 hour. This process was repeated until the desired amount of coating had been applied.

Degussa P25 Dip Coating

Degussa P25 was donated by Degussa Corporation. This is a mixture of approximately 15-30% rutile and 70-85% anatase, and is considered by some to be the gold standard of TiO_2 photocatalysis. A slurry containing 1.0 g/L P25 and 0.05 g/L dioctyl sulfosuccinate surfactant was used for dip coating the top side of the discs, with heat treatment as described above.

Evaluation of Activity

A series of screening tests were designed to identify highly active catalyst-support combinations. Because microorganisms and organic chemicals are key components of membrane fouling, our materials were submitted to screening tests for organic chemical oxidation and microbial disinfection. Materials that perform well in screening tests will be tested for fouling resistance in the next phase of this work.

Oxidation testing took place in a screening reactor illuminated by a 100 W mercury vapor lamp with peak intensity at 365 nm. A peristaltic pump continuously circulated 30 mL of 400 µM phenol, our model organic chemical, through the membrane filter. The phenol was allowed to adsorb for 30 minutes prior to illumination of the system. Samples were taken at 30-minute intervals for HPLC analysis of phenol concentration.

Pseudomonas putida, a common environmental biofilm former, was chosen as the model microorganism for microbial disinfection screening. A concentration of 10^5 cells/mL *P. putida* in phosphate buffer solution was illuminated in the screening reactor for 1 hour. The viability of *Pseudomonas putida* deposited on the filter discs was evaluated using a “live/dead” stain and confocal laser microscopy.

Results and Discussion

Results from phenol oxidation experiments are displayed in Figure 1, below. The discs exhibiting the highest activity include those coated with Degussa P25, and zirconia discs coated with sol gel anatase. Those exhibiting the lowest activity were sputtered samples.

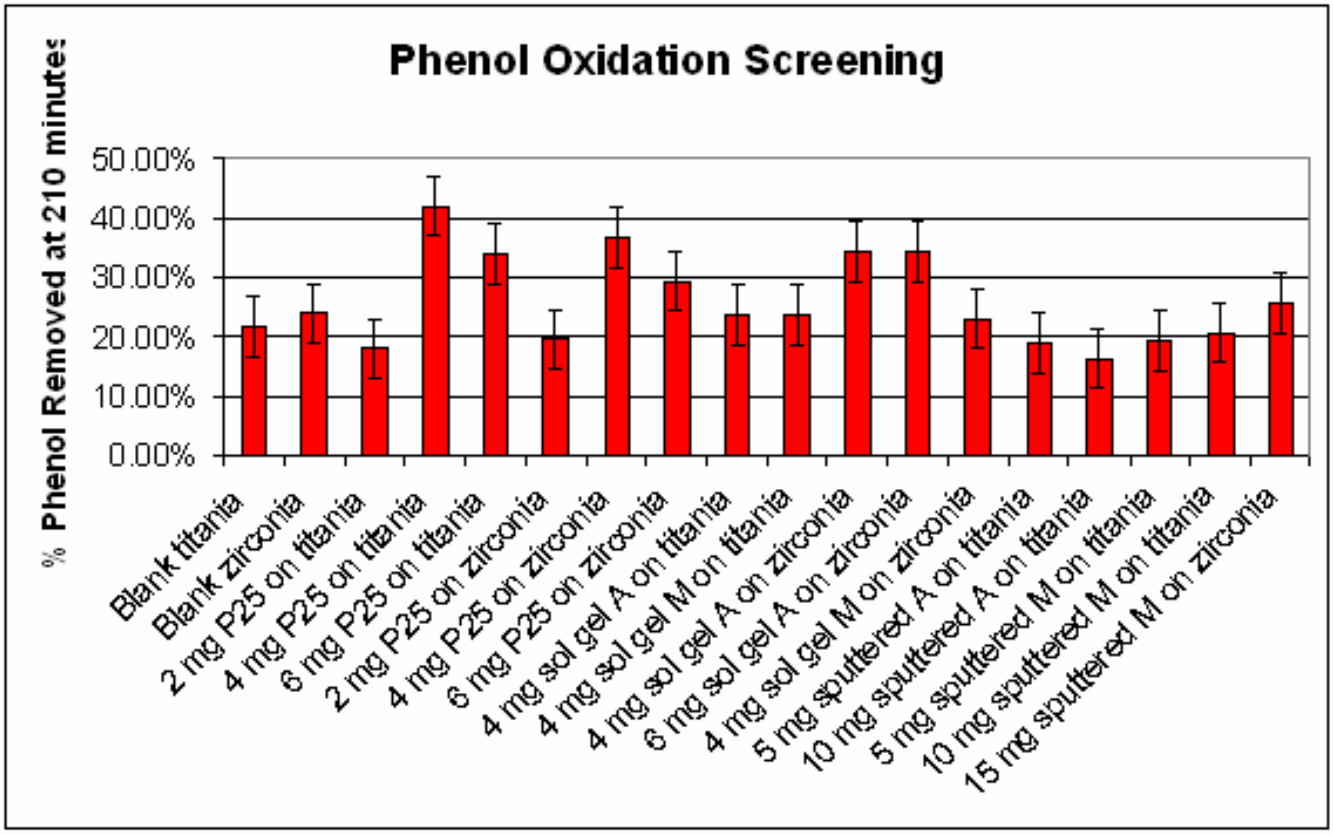

Figure 1. Results of phenol oxidation screening

As expected in heterogeneous catalysis, a catalyst loading effect was observed, most clearly in the results from discs coated with Degussa P25. As shown in Figure 2, adding more than 4 mg of P25 to our discs was not beneficial. The same was true of adding more than 4 mg of sol gel anatase and more than 5 mg of sputtered coatings.

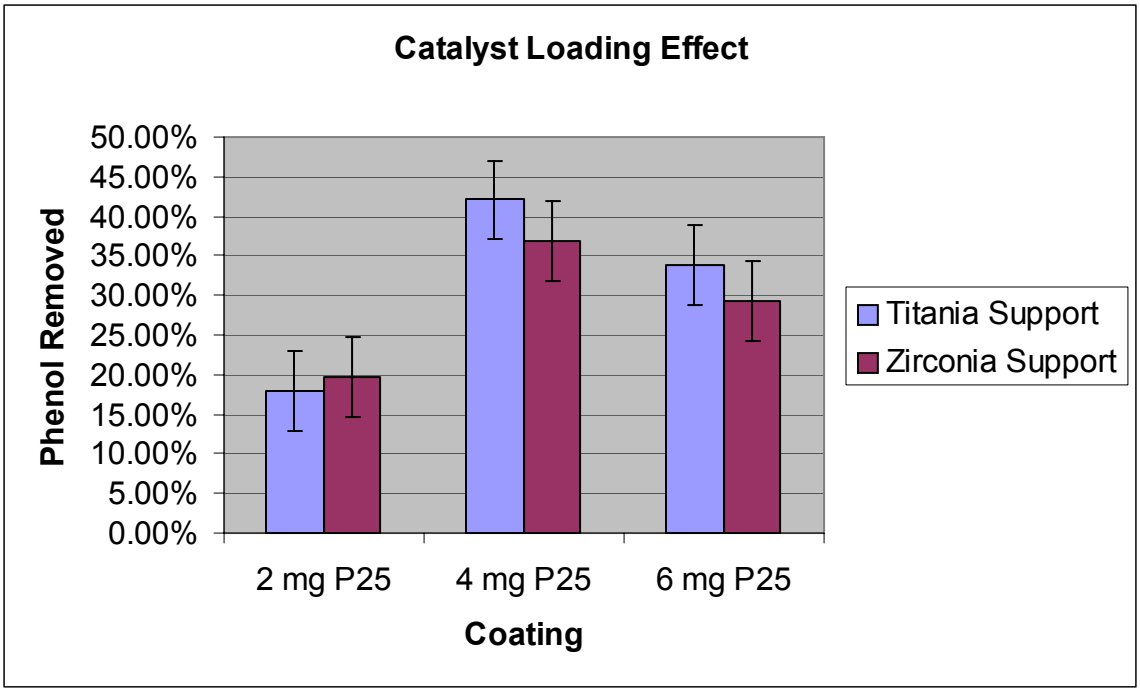

Figure 2. Catalyst Loading Effect

As shown in Figure 3, sol gel anatase outperforms sol gel mixed phase catalyst, and is comparable to Degussa P25, when supported on zirconia supports. These results were not expected, because previous testing of these catalysts for acetaldehyde degradation in air showed that the mixed phase sol gel catalyst was more effective than Degussa P25. A mixed phase “hot spot” may be forming at the catalyst-support interface in the anatase sample.

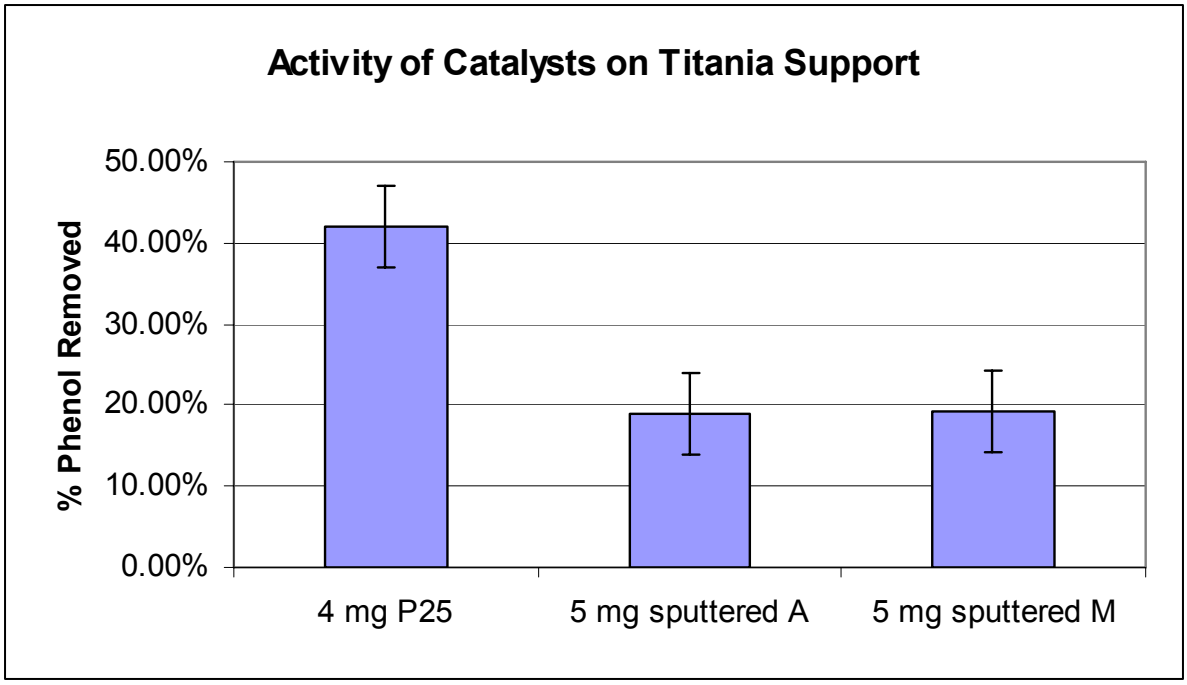

Figure 3. Sol gel anatase comparable to Degussa P25

The performance of sputtered coatings was surprisingly low. Figure 4 shows the comparison of similar weight loadings of P25 and sputtered anatase and mixed phase coatings. These results were somewhat surprising because the sputtered catalysts outperformed P25 in previous activity tests on the degradation of acetaldehyde in air. We attribute this low activity to the very dense nanostructure of the sputtered catalysts. Compared to the P25-coated samples, these catalysts have a much lower exposed surface area.

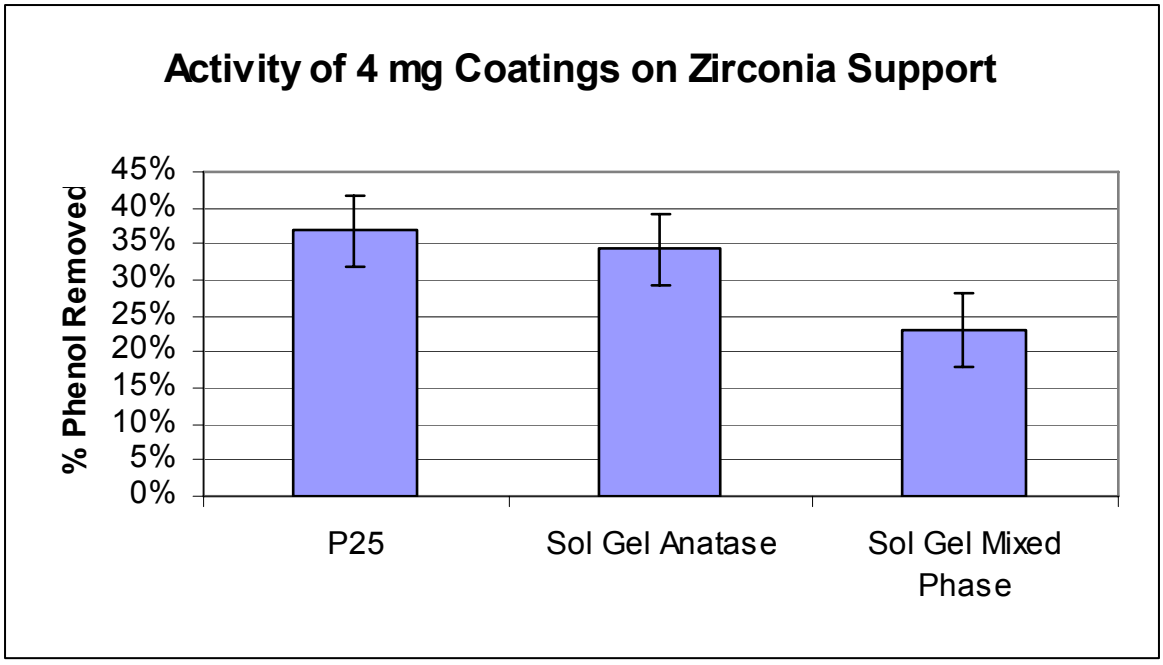

Figure 4. Sputtered coatings compared to P25 coating

Disinfection tests show that P25 is a strong microbial disinfectant. After 1 hour of illumination, at least 90% of *P. putida* cells in the P25 system had compromised cell membranes, compared to only 58% in the case of a blank support. Figure 5 displays the confocal microscope image of a slice from the center of the biomass on each of the discs. “Dead” cells with compromised membranes appear as red or yellow, while “live” cells with cell membranes in tact appear as green. Very few viable cells remain after illumination in the P25 system.

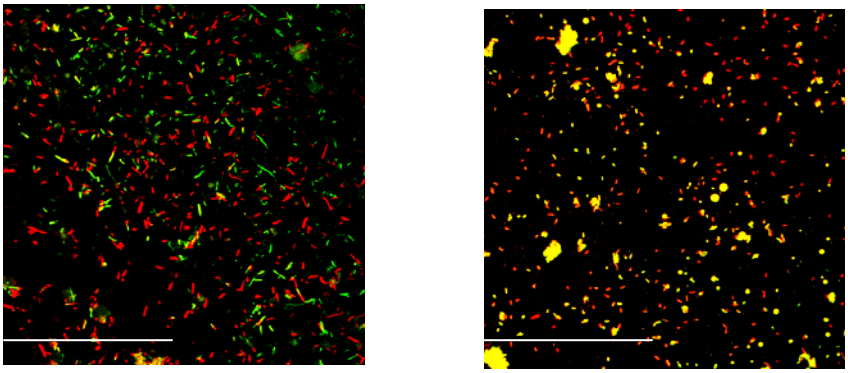

Figure 5. Confocal microscopy results (scale bar 75 μm)
a) Titania support b) P25 coating on titania support

While sputter-coated discs displayed low activity in phenol oxidation screening, preliminary results indicate that they have high disinfection activity. Figure 6 shows the comparison of a blank zirconia disc illuminated for 1 hour, and a zirconia disc coated with sputtered anatase. Results show that 58% of microbes are “dead” in the control sample, while at least 95% of microbes are “dead” in the sputtered sample.

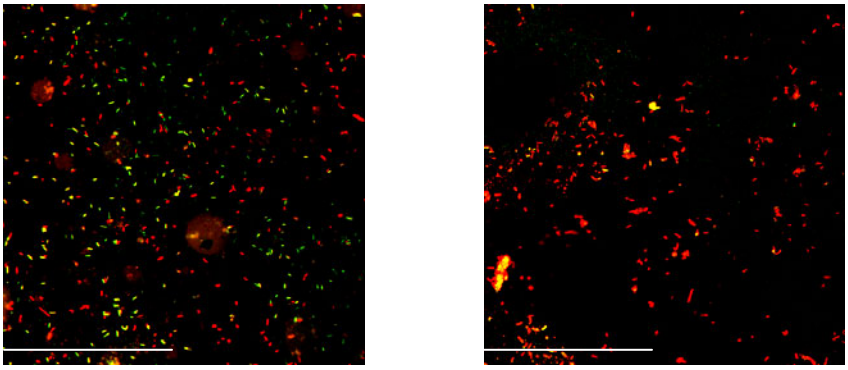

Figure 6. Confocal microscopy results (scale bar 75 μm)
a) Zirconia support b) Sputtered anatase on zirconia support

Our results indicate that dip coating is a better deposition method as measured by oxidation tests, while sputter coating may have advantages in disinfection. Degussa P25 shows strong activity in both types of screening tests. We think this is due in part to the morphology of samples. Interaction of catalysts with the support may generally have an inhibitory effect. Degussa P25 presents the most exposed catalyst surface area compared to other coatings tested, and may have a higher degree of catalyst-catalyst interactions as

opposed to catalyst-support interactions. In this case of membrane filter supported catalysts, the physical considerations may be more important than some details of the catalyst chemistry.

Acknowledgements

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