Preparation of Reusable PVA-Nano TiO_2 Foam For Wastewater Treatment

By Justin Huang

Abstract: With increasing industrialization, rapid economic development, and an ever-growing population, the problem of water pollution and water scarcity is increasing at an alarming rate. It is estimated that more than 800,000 annual diarrheal deaths are attributed to unsafe water usage. Traditional wastewater treatment technologies, such as adsorption, chlorination and biochemical methods are difficult for treating wastewater at low concentration thus leading to high toxicity. Nano TiO_2 based photocatalytic technology is a new high-efficiency and energy-saving wastewater treatment technology because nano TiO_2 can degrade organic pollutants into non-toxic compounds such as CO_2 and H_2O under the sunlight. However, one issue is on separation and recycling nano TiO2 from water. Therefore, we prepared PVA-Nano TiO_2 foam at high speed stirring, film laying, drying and thermal crosslinking. Thus TiO2 is embedded in PVA for reuse and recycle. The morphology, structure, and photocatalytic performance of PVA-Nano TiO_2 foam were characterized in detail by SEM, TGA, FTIR, UV-Vis and so on. The results show that TiO_2 nanoparticles have no effect on thermal crosslinking of PVA, the cell size of the foam is about .2-.5 mm, and the swelling degree of PVA-Nano TiO2 foam is about 600%. Under sunlight, the PVA-Nano TiO 2 foam possesses photocatalytic activity that is higher than that of non-porous PVA-Nano TiO 2 film due to the higher permeability of water and impurity with higher porosity. In addition, the PVA-Nano TiO_2 foam exhibits good reusability under multi-cycle use. This novel design of PVA-Nano TiO_2 foam is simple, eco-friendly, and effective with potential practical application value.

1. Introduction

Water pollution and scarcity is a growing issue globally. Water pollution in the form of plastics, toxic chemicals, and microorganisms causes harm to sea life in addition to limiting the supply of clean use and drinking water. It is estimated 1.5 billion people in developing countries are without safe drinking water (WHO 2014). Around 80% of wastewater is directly discharged into the ocean, river, or seas without any wastewater treatment, causing 1,000 children death each day due to preventable sanitation related diarrheal diseases. The United Nations 6th sustainable development goal is to obtain access to clean water globally.

In order to combat these issues, an environmentally friendly and cost-effective solution to help treat water easily and efficiently was sought. Currently some methods used to provide clean drinking water are chlorination, ozone, and filtration [1]. National Drinking Water Clearinghouse provides the pros and cons of each method. Chlorination provides a relatively cheap disinfection method, but it is corrosive or toxic to humans. Ozone treatment is expensive. Filtration cannot get rid of all the dangerous viruses in our drinking water.

A new method to treat water involves using the power of the sun [2]. New photocatalysts can use the energy from the sun to react with harmful microorganisms or harmful compounds. Titanium dioxide (TiO2), one of the most promising photocatalysts, has been widely used in the fields of air purification, sewage treatment, water splitting, reduction of CO2 , and dye sensitized solar cell, because of its low cost , nontoxicity**,** high photo stability and high photocatalytic activity [3]. The photocatalytic principle of TiO2 is shown in Figure 1. Under UV light, the electrons on the valence band of TiO2 are excited and transferred to the conduction band. Electron-hole pairs have strong redox ability and can activate oxygen and water to produce reactive oxygen and hydroxyl radicals, which can react with bacteria and other harmful pollutants into CO2, water etc [4].

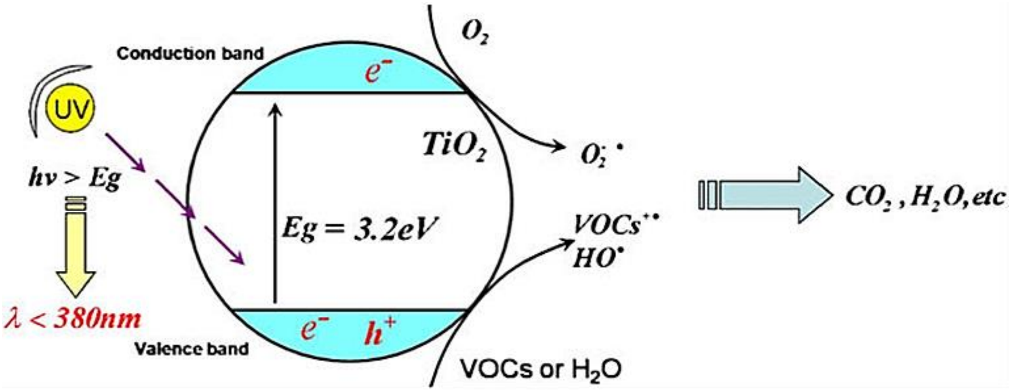


Fig. 1. schematic of the photocatalytic principle of TiO_2

Nano TiO_2 was more efficient due to higher surface areas. However, it was not able to be collected from water afterwards. The residue TiO2 in water can be a potential threat. In order to use TiO2 photocatalyst, a reusable and recyclable method needs to be invented. Recently substances such as glass, ceramics, PP, or PVA have been used to immobilize TiO_2 [5]. Shang et al [6] coated TiO2 on the surface of stainless steel wire mesh. Also TiO2 was loaded on formaldehyde. Hashemizad et al [7] immersed TiO2 and polyester. Lei et al [8] prepared PVA-TiO2 film and showed good results. Zhang et al [9] coated PVA/TiO2 on honeycomb ceramics and showed photocatalytic activity. However, using solids such as those limits accessibility of water impurity thus lower efficacy. A large surface area and open structure are the basic requirements to facilitate the diffusion of the reactants from the solution to the surface of the photocatalyst. Lee et al [10] prepared PVA/TiO2 by electrostatic spinning, Nguyen et al [11] prepared a porous PVA/TiO2 by freeze-drying. However, there are still many challenges in developing a cheap and eco-friendly method for the preparation of efficient, recyclable, and reusable photocatalyst.

When mixing eggs and when washing clothes, I realized that that the high agitation and the high rotation of the washing machine was able to bring air into the solution and create aeration and more air bubbles. By stirring the solution at a higher rate, we were able to stir in more air molecules. These air molecules were able to increase the porosity of the PVA-TiO_2 film. After creating these air pocket bubbles, the surface area of the foam increased. Herein, we prepared PVA-TiO2 foam through high speed mixing, film laying, drying and thermal crosslinking for invention. The morphology, structure, photocatalytic properties were characterized in detail via SEM, TGA, FTIR, UV-Vis, and more. PVA-TiO_2 foam we created showed photocatalytic performance under Sun light, proving potentials to purify water.

2. Experimental

2.1 Chemicals and Materials

PVA (3 types): MW 31-50k 98% hydrolyzed; MW 85-140k 98-99% hydrolyzed; MW 146-196k 99+% hydrolyzed

TiO_2 21nm with over 99.5% trace metal

Methyl orange (dye content 85%) was used as a model pollutant.

2.2 Preparation of PVA-Nano TiO_2 hybrid foams

Step 1: PVA solution preparation

Add 30g of PVA to a flask and then add 370g deionized water. After leaving the mixture for an hour, the beaker was put in an oil bath and mixed at approximately at 300 revolutions per minute. The temperature was raised to 95°C, allowing the solution to dissolve for 3 hours into a transparent PVA solution of 7.5%.

Step 2: PVA/TiO2 foam preparation

Put 0.3g of TiO_2 powder into a 150ml beaker with 5g deionized water. Ultrasound the mixture for 10 minutes. Add 40g 7.5% PVA solution. High-speed mechanical mixing at >1000r/min for 10 minutes to mix in air to produce foam. By mixing air into the solution it creates a foam with bubbles that the added air created. A large number of bubbles can probably increase the contact area between titanium dioxide and pollutants, and further enhance the photocatalytic activity of the composite catalyst. We pour the PVA/TiO2 solution on a horizontal Teflon plate, scrape it onto a thin film. After drying, we heated the foam inside a 140°C oven for 2 hours to get the cross linked PVA/TiO2 foam.

2.3: Characterization of PVA/TiO2 foam (SEM, FTIR, TGA, UV-Vis, et al)

PVA/TiO2 foam prepared above was characterized by SEM, FTIR, TGA, and UV-Vis. We used an FTIR machine to figure out the bonding and cross linking in our foam. The FTIR was able to scan for intramolecular bonding. An SEM was used in order to confirm the readings of the FTIR machine and to obtain pictures of the TiO_2 in the film before and after the foam formation. Originally a scanning light microscope was used, however Nano TiO_2 was too small to be seen in its field of view.

2.4: Evaluation of PVA-TiO2 hybrid foam's photocatalyst efficacy Photocatalytic degradation

Methyl Orange was used as a model contaminant for studying the performance of PVA-TiO_2 photocatalytic abilities. UV-3100 PC spectrophotometer VWR was used to measure the absorbance of the methyl orange solution in order to correlate the absorbance to the concentration of Methyl Orange. The change in concentration of Methyl orange was monitored using absorbance at 465 nm with a UV-Vis. The formula for % degradation is as follows: $\%\,degradation = \frac{C0-CT}{C0} \times 100\%$ where C0 is the initial absorbance and Ct is the absorbance of the contaminant solution at time t. The PVA-TiO_2 sample was then dried and re-measured in multiple trials.

3. Results and Discussion

3.1. PVA-TiO2 foam showed porosity / bubbles and TiO2 nano particles

Pictures, shown in Figure 2, were taken for pure PVA, PVA-TiO2 film formed at low mixing rate and PVA-TiO2 foam formed at high mixing rate. Results show significant air trapped into the foam with high porosity.

To better visualize and confirm the air bubbles in PVA-TiO2 foam, we took the microscope images for B and C, shown in Figure 3. The microscope was able to capture the increased porosity of the PVA-TiO_2 foam. Both samples contain the TiO_2 photocatalyst however as seen in the second microscope picture, the size of the pores are increased. This signifies that our process is able to increase porosity and therefore surface area. Results show the transformation of PVA between its pure form, with TiO2 as a film, and with TiO2 as a foam. The foam images clearly indicates the production of many pores that help increase porosity, thus allows water/impurity permeation and increased surface area.

One of the instruments needed for our experiment were Scanning Electron Microscopes in order to capture what our Nano TiO_2 looked like before and after the PVA transformation.Furthermore, SEM images were taken for PVA-TiO2 foam to confirm the embedded TiO2, shown in Figure 4 (A and B). As seen in this SEM of our Nano-TiO2 mixture, we can see the TiO2 wedged into the foam. This shows that our foam should be able to perform its photocatalytic abilities because it has the Nano TiO2 trapped within.

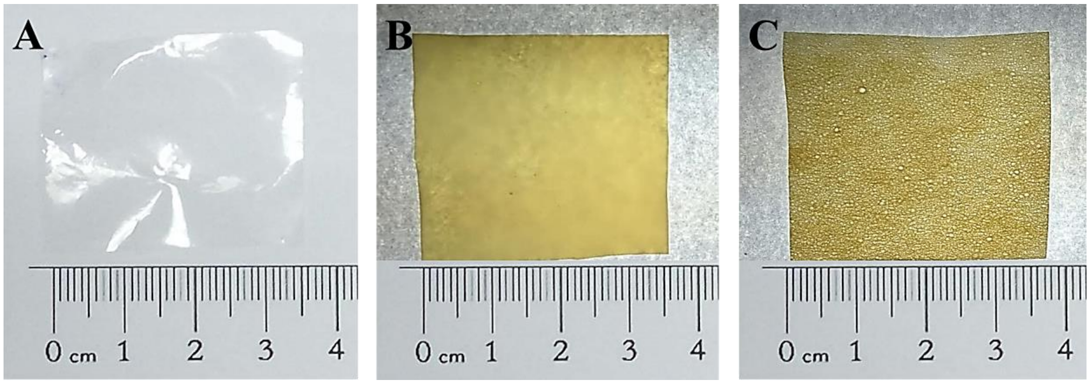
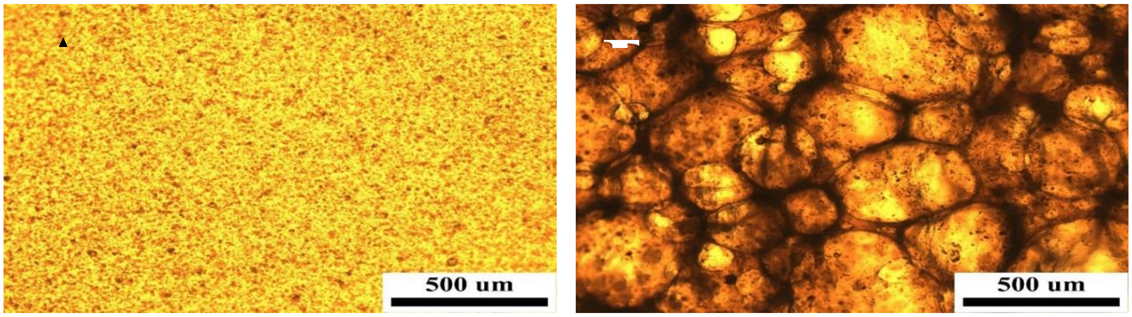


Fig. 2. Pictures of pure PVA (A), PVA-Nano TiO_2 film (B) and PVA-Nano TiO_2 foam (C)



B C

Fig. 3. Microscope images of PVA-Nano TiO_2 film (B) and PVA-Nano TiO_2 foam (C)

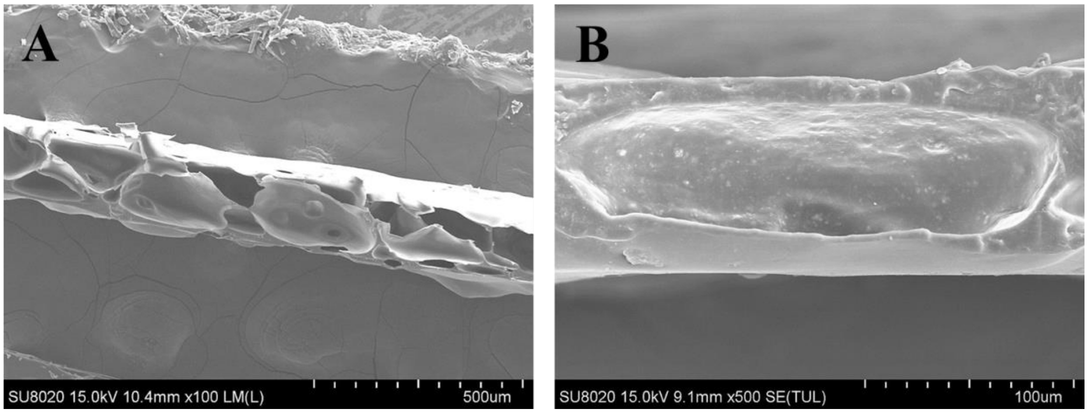


Fig. 4. Scanning Electron Microscope images of PVA-Nano TiO_2 foam (A and B)

3.2. TGA and FTIR indicates crosslinking temperature did not cause samples change

TGA (Thermal Gravimetric Analysis) was used to analyze the sample integrity and the results in Figure 5 showed that Pure PVA film, PVA-TiO2 film and PVA-TiO2 foam are very similar until at the end, where PVA-TiO2 film and PVA-TiO2 foam are similar as the residue is TiO2.

FTIR results in Figure 6 further proved that PVA bonding did not get impacted by crosslinking and the addition of TiO2 did not impact the PVA crosslinking either.

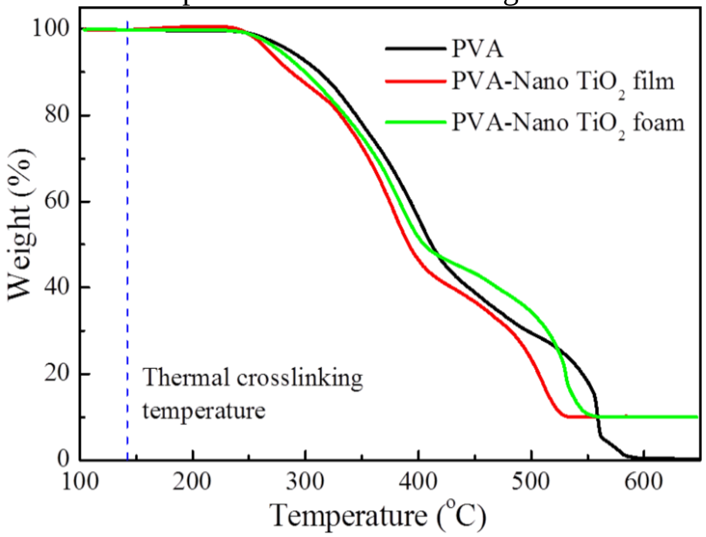


Fig. 5. TGA curves of pure PVA, PVA-Nano TiO_2 film and PVA-Nano TiO_2 foam

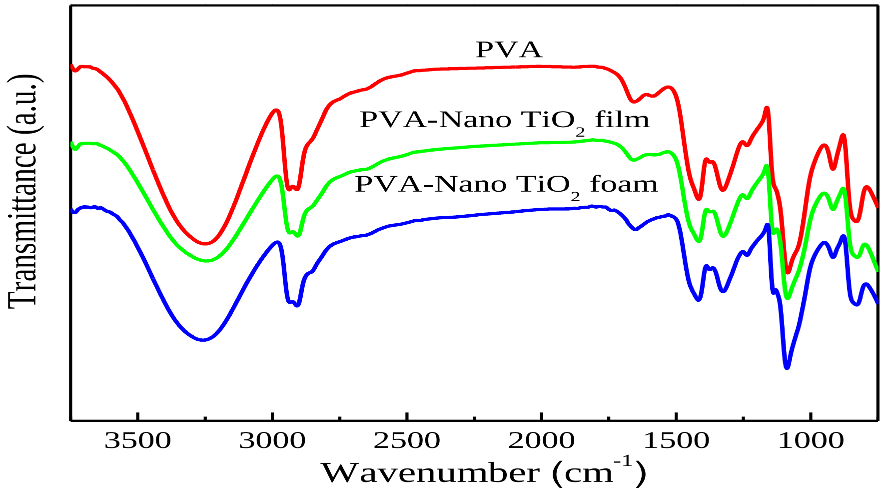


Fig. 6. FTIR spectra of pure PVA, PVA-Nano TiO_2 film and PVA-Nano TiO_2 foam

3.3. Swelling degree and sample density confirmed high porosity in PVA-TiO2 foam

We conducted swelling degree measurement on the sample by immersing in water and the results in Table 1 showed that PVA-TiO2 foam has the highest porosity (lowest density). We can see how the experimental process helps increase the surface area of the PVA-Nano TiO2 mixture. We see that the swelling of the PVA and PVA-Nano TiO2 foam change from 200% initially into 600% afterwards.

Table. 1. Swelling degree and density of the samples

Samples	PVA	PVA-Nano TiO_2 film	PVA-Nano TiO_2 foam
Swelling degree (%)	200	170	600
Density (g/cm^3)	1.17	1.25	0.26

3.4. Proposed high efficiency method to prepare PVA-TiO2 foam show success via UV-Vis

Our PVA-Nano TiO_2 film was produced successfully so that the TiO_2 is trapped inside. After many more experiments on how to create a better PVA-TiO_2 foam that is efficient and reusable, our method listed in the experimental part proved to be successful. In our data, it is clear that the TiO_2-PVA foam is still able to treat the pollutants such as the Methyl Orange used in this scenario. In the solution of TiO_2 without PVA we saw that the concentration of Methyl Orange decrease at a rate of 13 mg/L per hour while the solution with the ideal PVA foam had a rate of around 4 mg/L per hour. This is because although Polyvinyl alcohol (PVA) is a kind of water-soluble polymer material that can hold TiO_2 because of its hydroxyl groups, excellent film-forming, water-soluble, mechanical properties and biodegradability, we decided to apply it to our photocatalyst. Pure PVA film has no obvious absorption of UV and visible light and is very suitable for support nanometer TiO 2 photocatalyst. However, due to the slow water permeability of PVA after cross-linking, the pollutants could not contact with nano TiO 2 photocatalyst in time. Our data on photocatalytic measurement in Figure 7 showed PVA-TiO2 foam has significant higher photocatalyst performance than PVA-TiO2 film.

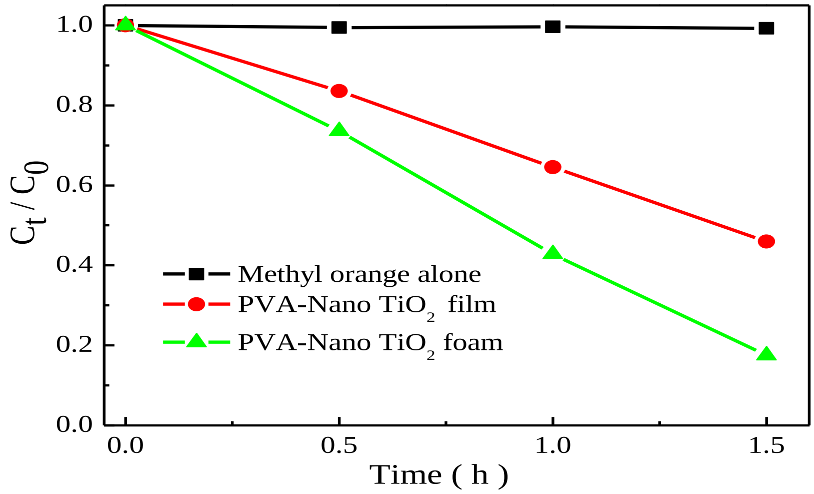


Fig. 7. Photocatalytic degradation of Methyl orange solution under simulated sun light

After creating the PVA foam, we were able to see that the PVA was an efficient way to get rid of the pollutants. The PVA-TiO_2 is able to dispose of the same number of pollutants over a longer stretch in time (table 1 and 2). The reusability of the PVA-TiO_2 however is much better than just using the nano-TiO_2 particles alone. With no difference in mass before and after the experiment, 100% of the PVA-TiO_2 foam's mass is retained allowing us to use the foam again. Although a longer time will be required, I will eventually discuss methods that can be done to reduce the time taken to reduce pollutant. Also, the PVA-Nano TiO_2 is able to be used well as a photocatalyst due to the foam containing the TiO_2 particles mixed throughout as seen through our microscopic images. As seen in the Figure 7, the foam was much more effective than the film. This product will be able to expand on the innovation of PVA and TiO2's synergy. Although it is unable to remove solid waste, this product can turn freshwater into clean, safe, and drinkable water by removing pollutants that are in small concentrations but extremely toxic.

3.5. PVA-Nano TiO2 foam was easy to recycle and reuse

Our PVA-TiO_2 foam was able to be reused and recycled after being baked in the oven until dry again. After recharging the TiO_2 by using UV light and energy, the TiO_2 foam is ready to be used again. After reusing the same TiO_2 foam in multiple trials, we found out that the performance was around the same. Not only is the TiO_2 able to effectively degrade highly concentrated pollutants but it is able to be recycled.

As shown, PVA TiO2 was unaffected by multiple trials showing the same performance in almost all 5 trials. The bubbles helped increase the performance of the foam allowing it to degrade more than 90% of the pollutant. Our TiO2 is more effective than normal thanks to the addition of surfactant, higher stirring rate, and finally baking at lower temperatures. These 3 factors come together to create a better version of the nano foam that can be reused and work efficiently.

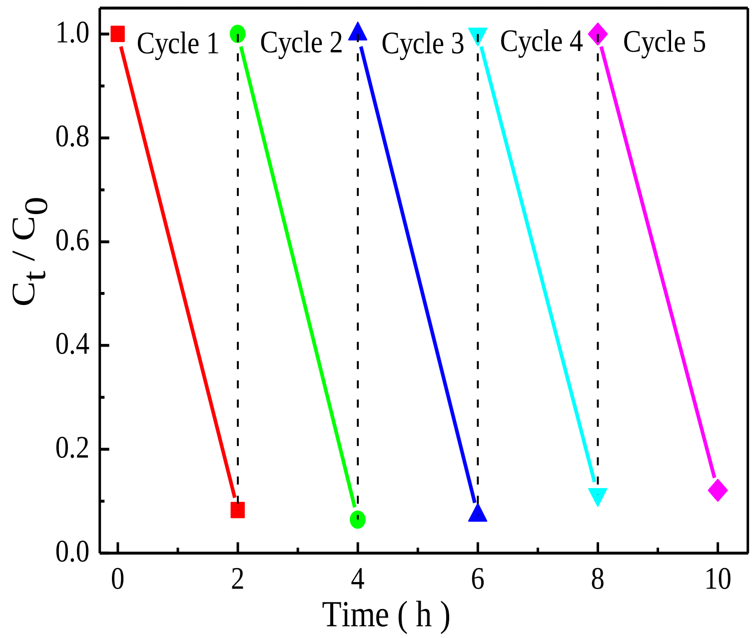


Fig. 8. Recycle photocatalytic performance test of PVA-Nano TiO_2 foam

3.5. Optimization PVA-Nano TiO2 foam efficacy under various parameters and conditions

To improve the performance of the new invention, the hypothesis is, if we can increase the permeability and the effective surface area, the performance will be improved. A few approaches were explored and the results are showing in Figure 8 and Table 2.

3.5.1. Lower PVA MW results to higher efficacy As PVA MW increases, it is possible becoming more difficult to access TiO2. Three MW PVA was tested and lowest MW PVA had the best performance.

3.5.2. *Use foaming agent to increase the aeration* When foaming agent was used, it creates more bubbles and thus increases the foam porosity and potentially contributes to higher surface areas and easier access. Less than 0.01% SLS was used and showed increased performance. Figure 8 Visibly showed pore sizes in the PVA foam with the foaming agent are much larger meaning that the surface area of the foam will be larger and so will the photocatalytic ability of the foam. This is probably because when we mix in air after adding a surfactant, we are able to reduce the surface tension of the liquid mixture. A surfactant is able to align itself in such a way that the hydrophobic tails will be out of the liquid while the polar heads will be in the liquid, this way the surfactant is able to break these intermolecular forces and interactions When reducing the surface tension, we decrease the interactions between the water molecules on the surface of the liquid allowing for more air to be mixed in more easily. This is important because more air in the solution creates more bubbles and a higher surface area and more effectiveness.

3.5.3. Lower the drying temperature to optimize the performance With lower temperature, less bubbles claps and less crosslinking degree, both can potentially increase the access-ability and surface areas of the effective photocatalyst. We tested at 60°C instead of 140°C. It was discovered that by drying the foam at a lower temperature it would be more effective.

3.5.4. *Lower the drying time to enhance the performance* Similar mechanism to drying temperature. Take it out after cross linking for 30 minutes in the vacuum state rather than 2 hours, higher performance PVA/TiO_2 foam was produced.

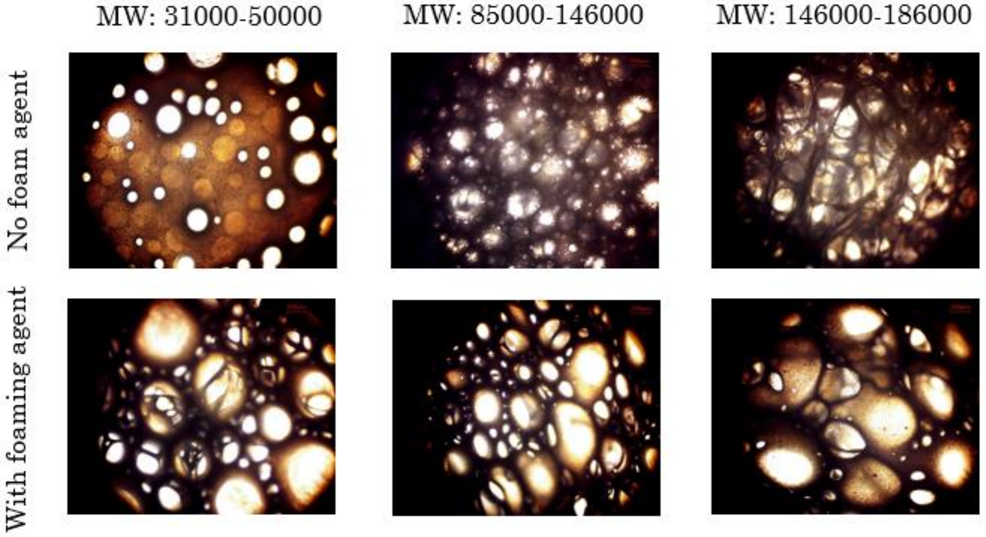


Table 2. Photocatalyst performance of PVA-Nano TiO2 at different conditions

(vs. Base – PVA-Nano TiO2 MW 31-50k, drying 2 hrs at 140°C without foaming agent)

Conditions	Performance index (vs Base)
PVA MW 31-50K	1.00
PVA MW 85-140K	0.87
PVA MW 146-196K	0.68
Addition of foaming agent	1.55

Drying at lower Temp. (60°C vs. 140°C)	3.10
Drying for shorter time (0.3 vs 2 hr)	1.32

3.6 Broadened applications of PVA-Nano TiO 2 foam

This PVA-TiO_2 hybrid foam can be applied in many instances such as water bottles, water treatment plants, or being used in communities without freshwater such as Flint, Michigan.

3.7 Recommendation for industrialization

In order to apply this to industrialization, we would need to apply this film into waste water plants as a final step. Although the wastewater treatment has Fluoride and Chloride, our PVA-TiO_2 foam is able to do the same job and be reused many times without need for repair. By using our PVA-TiO_2 foam in such systems in third world countries, we can make a big difference in their availability of clean water.

4. Conclusion

The TiO2-PVA film was successfully synthesized using the procedures above at very high stirring rate. The photocatalyst had improved capabilities and was able to be reused in multiple cycles. The higher surface area enabled the foam to perform better enabled by the increased number of pores. In addition, the usage of a foaming agent, lower molecular weight PVA, lower drying time, and lower drying temperatures help increase the porosity and permeability of the PVA foam; however the integrity and re-usebility is unknown and needs to be further studied and explored. The new formation method for the PVA-TiO2 foam can be applied and used in water treatment plants or water pumps so we can provide more fresh water to serve the world increasing population. While going through our methods of producing the PVA-TiO_2 foam we discovered new ways to improve upon the method for industrialization such as using different molecular weights of PVA, baking at different temperatures, or mixing in a surfactant.

First we tried testing out the effectiveness of using PVA of different molecular weights alongside the original molecular weight used. We compared PVA with molecular weight 31000 to 85000, and 146000. We found that the lower the molecular weight of the PVA, the degradation rate of the Methyl Orange would be faster. Afterwards we tried testing out the baking temperature of the final PVA-TiO_2 film. We found out that the lower the final baking temperature of the PVA-TiO_2 film before use and before reusing, the higher the degradation rate of methyl orange. This PVA-TiO_2 foam is ideal for our purposes because it is able to degrade large percentages of small concentration but highly toxic products such as DDT or Viruses. If we are able to degrade a large percentage of these toxic particles with only 40mg of PVA-TiO_2 and we are also able to conduct many experiments using the same film consecutively with almost 0% change in mass. This shows that the product we set out to create a product that could be mass produced easily at a cheap price, has been successfully prepared. Using our production method we could create PVA-TiO_2 that could provide clean drinking water by degrading low concentration toxins that could cause infection or death and be used many times.

5. References

[1] Betancourt W Q , Rose J B . Drinking water treatment processes for removal of Cryptosporidium, and Giardia. Veterinary Parasitology, 126 (2004) 219-234.

[2] Zhang H., Lv X., Li Y., Wang Y., Li J., P25-Graphene Composite as a High Performance Photocatalyst, ACS Nano, 4 (2010) 380-386.

[3] Li G., Wang F., Liu P., Chen Z., Lei P., Xu Z., Li Z., Ding Y., Zhang S., Yang M., Polymer dots grafted TiO_2 nanohybrids as high performance visible light photocatalysts, Chemosphere, 197 (2018) 526-534.

[4] Mo J., Zhang Y., Xu Q., Lamson J.J., Zhao R., Photocatalytic purification of volatile organic compounds in indoor air: A literature review, Atmospheric Environment, 43 (2009) 2229-2246.

[5] Coutinho C A, Gupta V K. Photocatalytic degradation of methyl orange using Polymer/titania microcomposites. J Colloid Interface Sci, 333(2009) 457-464.

[6] Shang J., Li W., Zhu Y., Structure and photocatalytic characteristics of TiO_2 film photocatalyst coated on stainless steel webnet, Journal of Molecular Catalysis A: Chemical, 202 (2003) 187-195.

[7] Hashemizad S , Montazer M , Rashidi A . Influence of the surface hydrolysis on the functionality of poly(ethylene terephthalate) fabric treated with nanotitanium dioxide. Journal of Applied Polymer Science, 125 (2012) 1176-1184.

[8] Lei P., Wang F., Gao X., Ding Y., Zhang S., Zhao J., Liu S., Yang M., Immobilization of TiO_2 nanoparticles in polymeric substrates by chemical bonding for multi-cycle photodegradation of organic pollutants, Journal of hazardous materials, 227 (2012) 185-194.

[9] Zhang J., Yang H., Jiang L., Dan Y., Enhanced photo-catalytic activity of the composite of TiO_2 and conjugated derivative of polyvinyl alcohol immobilized on cordierite under visible light irradiation, Journal of Energy Chemistry, 25 (2016) 55-61.

[10] Linh N.T.B., Lee K.H., Lee B.T., Fabrication of photocatalytic PVA-TiO_2 nano-fibrous hybrid membrane using the electro-spinning method, Journal of Materials Science, 46 (2011) 5615-5620.

[11] Song Y., Zhang J., Yang L., Cao S., Yang H., Zhang J., Jiang L., Dan Y., Rendu Le, Nguyen T.P., Photocatalytic activity of TiO_2 based composite films by porous conjugated polymer coating of nanoparticles, Materials Science in Semiconductor Processing, 42 (2016) 54-57.