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Preliminary Study of Various Photoactive Nanomaterials for Oil Cleaning Application

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Authors' contributions

This work was carried out in collaboration between all authors. Author SZ managed the literature searches, experimental process and wrote the first draft of the manuscript. Authors BYD and CSB managed the data collection. Author YXG designed the study. All authors read and approved the final manuscript.

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ABSTRACT

In this paper, nanomaterials were tested for oil cleaning application. Comparative studies were performed on pure titanium, titanium dioxide nanotube, titanium dioxide nanoparticles embedded in electrospun polyvinylpyrrolidone (PVP) fiber that was heat treated and not heat treated, and titanium-cobalt oxide in PVP that was heat treated. The ability of these materials of decomposing and removing oil under photon energy excitation was evaluated. Ultraviolet (UV) light was used as the photon energy source to excite these nanostructured materials. It is found that the titanium oxide nanotube has the highest photon responsive activity. Other nanomaterials including heat treated oxide containing PVP fiber also shown the function of oil removal.

Keywords: Photoactive nanomaterials; oil cleaning application; oxide nanomaterials; nanotubes; nanofibers.

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1. INTRODUCTION

Oil removal systems using membranes and nanotubes have been a growing topic of interest in research. TiO_2 nanotube catches particular interest of researcher because of its high photocatalytic activity and amphiphillic property [1]. TiO_2 nanotube arrays were fabricated though electrochemical oxidation of Titanium in solution containing Ammonium fluoride. When compared to other types of photo-catalysts, TiO_2 is one of the best photo-catalysts because of its chemical stability and excellent charge transport property [1]. When TiO_2 is exposed to UV radiation, it reacts with oxygen and water molecules present in the atmosphere to produce free radicals. These radicals allow the decomposition of organic materials such as vegetable oil.

The study of nanofibers has attracted much attention because there are a wide range of potential applications. These nanostructures are potentially useful in biomedical applications such as sensors and a drug delivery system [2]. These nanofibers were also studied for the application of oil and water separation [3]. The ability of the nanofibers to decompose vegetable oil were investigated and compared to TiO_2 nanotube's ability to decompose vegetable oil. PVP can be easily dissolved in solvents to form solutions for electrospinning [4]. Titanium oxide particles and cobalt were added to the solutions and electrospun using a syringe and pump. Factors that determine the properties of the nanofiber are flowrate, voltage and distance from the syringe to the collecting surface [5].

Heat treatment of electrospun nanofibers improves the membrane compactness, mechanical property, chemical stability of the material [6]. The titanium cobalt nanofiber with PVP was heat treated and compared to nanofibers that were not heat treated for their ability to decompose organic material. The aims and objective of the work include to make the nanomaterials, to test the photosensitivity, and to identify the material with the highest wettability with oil.

2. MATERIALS AND EXPERIMENTAL

2.1 Materials

Vegetable oil was used as the organic material to be decomposed. Different types of materials containing Titanium were investigated. The control used was a clean piece of glass slide. The materials used were pure Ti, TiO_2 nanotube, electrospun TiO_2 with polyvinylpyrrolidone (PVP) nanofibers that was heat treated and non-heat treated, and titanium and Cobalt nanofibers with PVP that was heat treated. The stirrer time used in the preparation of Ti-Co-O and TiO_2 with PVP was half an hour. A 4 Watt UV light was used as the source of UV lighting and can be seen in Fig. 1. A clean dropper was used to transfer the oil onto the surface of the materials.

Fig. 1. UV light excited photodecomposition test set-up

2.2 Preparation of the TiO_2 Nanotube Photosensitive Anode

The nanotube was prepared a similar to research from Zeng et al. [1] by electrochemical oxidation but with ammonium fluoride. Using two Ti sheets for a cathode and anode and a voltage was supplied to the two-electrode cell. Electrochemical oxidization or etching of Ti to form TiO_2 nanotubes was carried out at the room temperature of 25℃. The distance between the two electrodes was 20 mm. The operation voltage was 50.0 V and the electrochemical oxidization time was 2 hours. After the electrochemical oxidization, the nanotube sample was rinsed in water and air dried. The surface of the anode was completely covered by TiO_2 nanotube arrays as revealed by the color change of the surface. For some specimen, after the TiO_2 NTs were prepared, high temperature annealing at 450℃ for 2 hours was conducted to crystallize the TiO_2. The electrochemically oxidized specimens with and without heat treatment were used to make the photosensitive anodes. Oil drops were set on the anodes for photochemical decomposition tests.

2.3 Preparation of Ti-Co-O and TiO_2 Nanoparticle in PVP (Heat Treated vs Non-heat Treated)

The following method was used to prepare cobalt and titanium oxides. A small beaker was set on a balance that was reset to zero. The following solutions containing various substances were made using the beaker. 0.13 gram of cobalt (II) acetate tetrahydrate, ($C_4H_6CoO \cdot 4H_2O$ with Co 24 wt%), 0.1 gram of 17.4 M acetic acid, 0.17 gram of titanium (IV) n – butoxide, ($C_{16}H_{36}O_4Ti$ with 99 + % purity), 0.75 gram of polyvinylpyrrolidone powder $(C_6H_9NO)_n$ with the molecular weight of 1,300,000 g/mol and 6.8 grams of ethanol(C_2H_5OH) with the ACS purity of 94–96% were mixed in the beaker and the solution was stirred to help the solid substances to dissolve into ethanol. Titanium oxide containing PVP solution was also made using the similar process. This solution made was then transferred into a syringe pump to be electrospun into the nanofibers. This is shown in Fig. 2 from previous research done with Kim et al. [4]. The nanofibers were heat treated for two hours at 500℃.

2.4 Characterization

The six materials were laid out on a flat surface that was exposed to UV light which can be seen in Fig. 3. The UV light was placed about 5 inches above the materials so that the amount of UV light exposed would cover the entire surface area of the materials. A clean dropper was used to place one drop of vegetable oil on each material. The material with the oil droplet was exposed to UV light for different time durations and the observations were recorded. The time intervals for UV light exposure were 5 minutes and 10 minutes. Photos of the oil drops setting on specimens after each trial were taken and shown in Figs. 4 to 11. The contact angle was also calculated based on the spreading area after each time increment. A Hitachi scanning electron microscope (SEM) was used to observe the surface of the heat treated nanofiber specimens. A typical SEM image was captured and shown in the Results and Discussion section.

3. RESULTS AND DISCUSSION

It can be seen in the following figures that TiO_2 nanotube is clearly the best material that should be selected for an oil cleaning system. After the three trials of UV light exposure with time increments of 5 minutes and 10 minutes, it can be observed that the vegetable oil on the TiO_2 nanotube was most widely spread and have the smallest amount of contact angle. This is due to its porous structure and the capillary effect taking place. It can be seen that the more spread out the oil droplet on the material, the smaller the contact angle is on the slide. The second best organic material decomposer would be the titanium and cobalt mixture of the PVP nanofiber that has been heat treated. It can be observed that the vegetable oil has a nice spread throughout the investigation and the size of the oil that spread was much larger compared to the TiO_2 with PVP nanofiber that was non heat treated and heat treated. When compared to pure Titanium, the TiO_2 with PVP that was non heat treated and heat treated are better organic decomposers. This result makes sense because there is fiber for the oil to penetrate where as pure titanium does not have this. However, these materials would still not be the most ideal selection for an oil cleaning system. The TiO_2 PVP fibers that were non heat treated seemed to be better at oil decomposition because it spread out much more than the TiO_2 PVP fibers that were heat treated. Since it is more spread out, it can also be seen that the contact angles were much smaller too. For all types of materials, the contact angle decreased as the exposure of UV light increased with time which was expected.

Fig. 2. Electrospinning setup

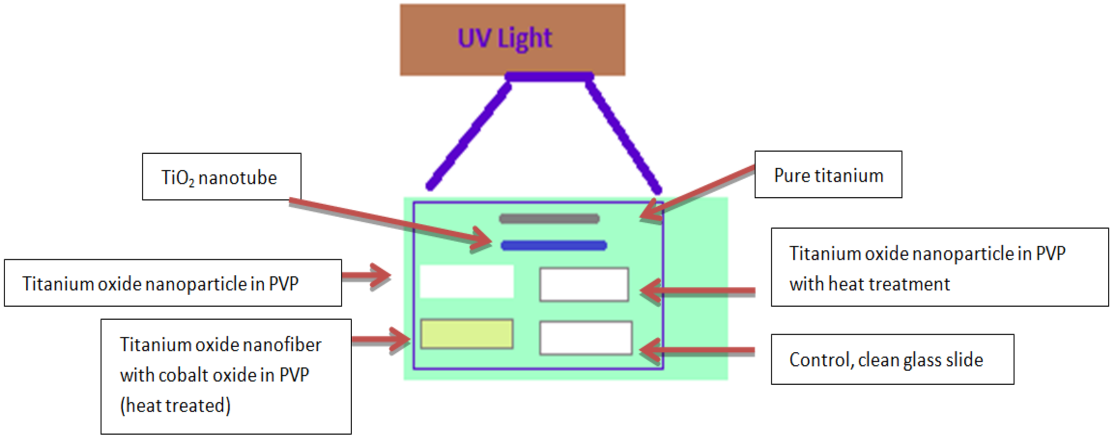

Fig. 3. Schematic of the experimental setup and the sample labeling

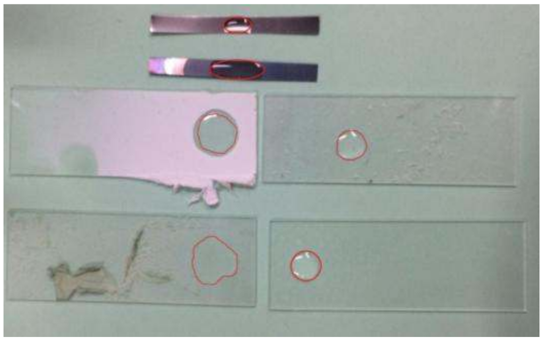

Fig. 4. Initial top view

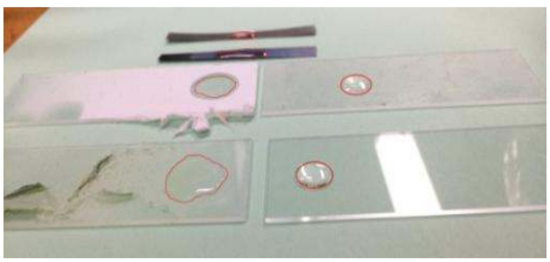

Fig. 5. Initial contact angle view

Figs. 4 and 5 illustrate the initial top view and side view of the oil drops on the surface of the six specimens. It is found that the shape of the oil drops is almost circular at the beginning. The oil drop with the least contact angle with the clean glass slide is calculated about 40° by using the method shown in [1]. After the 5 min exposure to the UV light, the oil drop on the titanium oxide nanotube specimen increased to about 160°, indicating the almost completely wetting case. The contact angle between the oil drop and the titanium is kept at about 60°. The two nanofiber specimens show some wettability with the oil drops, but they are not as good as the titanium nanotube. The contact angle of the oil drops on the nanofiber specimens is about 130° by calculation.

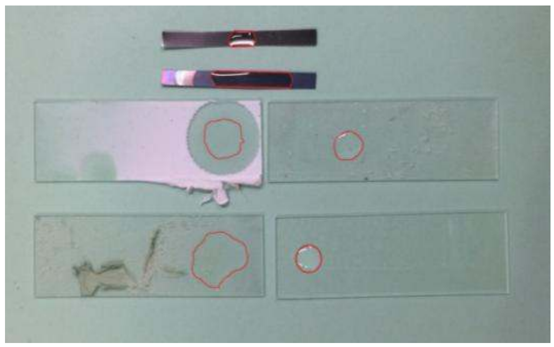

Fig. 6. Top view after 5 minutes

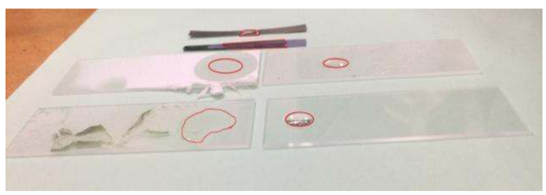

Fig. 7. Contact angle side-view after 5 minutes

It can be seen in Figs. 6 and 7 that just after 5 minutes of exposure to UV light, there was dramatic change in the contact angle of the TiO_2 nanotube but not too much change in the other materials. The calculated contact angle of oil with the TiO_2 nanotube is about 160° at this stage.

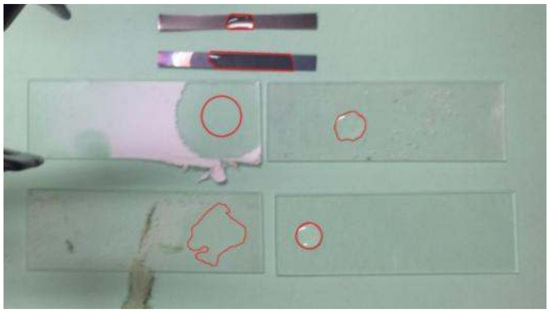

Fig. 8. Top view after another 5 minutes

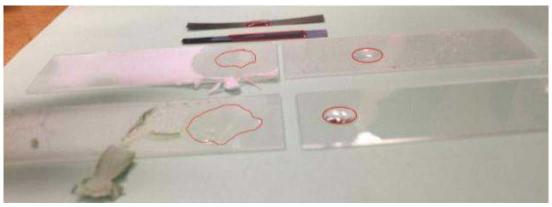

Fig. 9. Contact angle view after another 5 minutes

After another 5 minutes of exposure to UV light, the oil on the TiO_2 nanofiber with PVP that is nonheat treated was more widely spread and the contact angle of the heat treated titanium cobalt PVP nanofiber had also increased as can be seen from Figs. 8 and 9. There are two different mechanisms. Without heat treatment, the PVP polymer, due to the organic nature and in the texture state [7], it can partly absorb the oil. That is why the contact angle increases significantly with the time increasing. After heat treatment, the PVP fiber started changing in thermal and electrical properties due to the carbonization [8]. The carbonization also causes the shrinkage of the fiber and the inside nanoparticles expose to surface [9]. The nanoparticles including the titanium dioxide and the cobalt-titanium oxide with active photocatalytic property take the role in decomposing the oil drops. Therefore the wettability of the heat treated nanofiber is improved and it shows relatively high photosensitivity.

After another 10 minutes of UV light exposure, it can be seen from Figs. 10 and 11 that the material that has the best decomposition of organic material is still the TiO_2 nanotube. The next best material for oil removal is the titanium cobalt PVP nanofiber. Throughout the experiment, it can be seen that little to no change occurred to the pure titanium and the control sample (the clean glass slide). As a summary of the data, Table 1 lists all the time dependent wettability angles for the six specimens.

Table 1. Time–dependent wetting angle of oil on different specimens under UV irradiation

Specimen	**UV light irradiation time (minute)**			
	0	**5**	**10**	**30**
1 (Ti)	0°	40°	40°	40°
2 (TiO_2 nanotube)	0°	160°	165°	168°
3 (TiO_2-PVP)	0°	79°	103°	114°
4 (TiO_2-PVP heat treated)	0°	57°	77°	92°
5 (TiO_2-CoO-PVP heat treated)	0°	69°	88°	109°
6 (Glass slide)	0°	0°	0°	0°

In order to confirm the carbonization caused shrinkage of the fiber and the exposure of inside nanoparticles, scanning electron microscopic examination was performed on the heat treated PVP fibers containing oxide nanoparticles. As shown in Fig. 12, the titanium dioxide nanoparticles have lower electrical conductivity than the carbonized PVP fibers. Therefore, they look like white spots in the image. The size of the particle is less than 1 micron, which reveals the existence of nanoparticles embedded into the fibers.

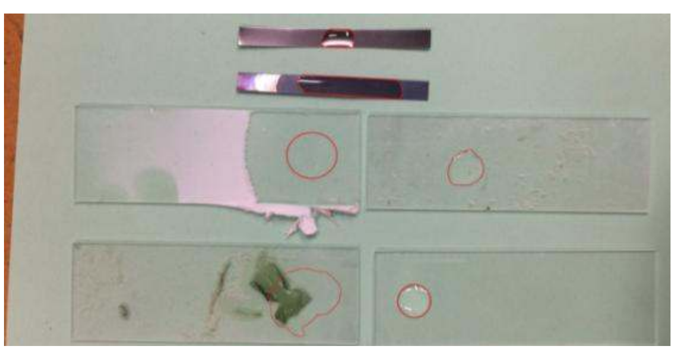

Fig. 10. Top view after 10 minutes

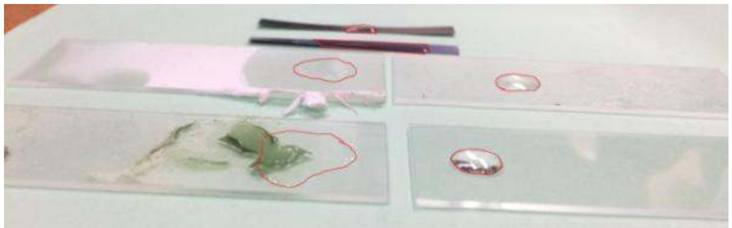

Fig. 11. Side view after 10 minutes

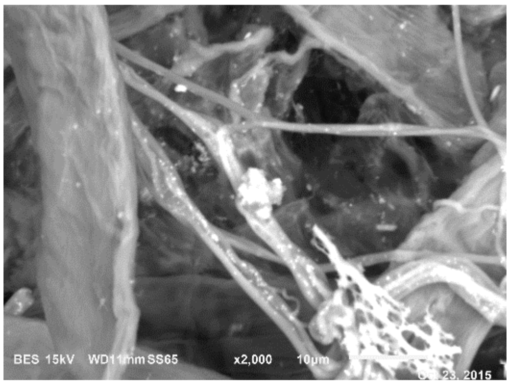

Fig. 12. SEM image showing the exposure of nanoparticles from the electrospun fibers

4. CONCLUSIONS

From the photosensitivity test and oil decomposition analysis, it is concluded that the TiO_2 nanotube is the best material among the five nanostructured materials tested. Decomposition of organics such as vegetable oil is validated for the nanostructured materials. The contact angle of the oil drop on the titanium dioxide nanotube sample starts change after 5 minutes excitation by the UV light. The contact angle of the oil drop on the titanium dioxide nanotube sample was 40^o at the beginning. It increased to 160^o after 5 minutes UV irradiation. The longer the exposure time, the bigger the contact angle is. This indicates that TiO_2 nanotubes are active under photon energy excitation. It is the best material for decomposition of organics among all the nanomaterials tested. Due to the chemical stability and excellent transport property of these nanomaterials tested, they have a great potential for oil decomposition and removal application. The manufacturing processes described in this work are scalable for large scale production of nanofibers and nanotubes.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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