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# Electrospun Titanium Dioxide Fibres for POME Treatment

Wan Dung Teng[1] and Nassya Mohd Said[1]
[1]Advanced Materials Research Centre, SIRIM, 40700 Shah Alam, Malaysia

***Abstract***: *Nanotitania has been developed as photocatalytic materials capable of self-cleaning, air purification, water purification, anti-bacteria, anti-fungus and other functions. Nanoparticles have been drawing the researchers and governmental officials' attention on the nano risks. It is a very challenging and expensive task to gauge and study the nano risk. In view of this, nanotitania was synthesized and prepared as suspension with PVP solution. The mixture was set to electro-spining into fibre at 18kV. The e-spun fibre was subjected to differential thermal analysis to obtain the sintering profile for obtaing sintered titania fibres. The titania fibres were sintered at 500$^oC$. The sintered phases and microstructural of titania fibres were analysed by using X-ray diffractometer and scanning electron microscope. The electrospun coated nanotitania fibres had shown low contact angle and reduction of COD in the POME treatment process.*

***Keywords:*** *Electrospun, Nanotitania, photocatalyst*

## 1. Introduction

Nanotitania is widely accepted as one of the photocatalyst materials on the market today [1-4]. Photocatalyst is a material that enters a high-energy state by absorbing photoenergy, then emitting energy to a reactive substance, promoting a chemical reaction. Titanium dioxide is a typical ceramic when light is applied; it creates electrons and positive holes. These electrons and positive holes create very strong oxidizers, known as hydroxide radicals. Therefore, it is widely used in self-cleaning, air purification, water purification, anti-mould, and others.

This titania is in the form of nanoparticle. Nanoparticles have been drawing the much researchers and governmental officials' attention on the nano risks. It is a very challenging and expensive task to gauge and study the nano risk. By utilizing electrospinning technique on the possibility of producing a cross-linked nanotitania fibre web-like structure, this may reduce the nano risk as compared to the nanoparticles or individual nanofibres. Ceramic nanofibres of alumina-borate, titania, zirconia have been fabricated in previous studies [5-7]. However there is dispute as to the anatase-rutile phase transformation at higher temperature and grain growth [8,9].

Electrospinning has been known since the 1930's for polymer fibre production. The principle of electrospinning is to use a high voltage electric field to draw a positively charged polymer solution from an orifice to a collector. This creates a cone-jet of solution from the orifice to the grounded collection device. Then it travels to form a stretched jet, whipping motion, and then forms fibres collected on a grounded metal plate. By using electrical forces, the electrospinning process can produce fibres with nanometer diameters. Because of their small diameters, electrospun fibres have drawn great attention for fabrication of ceramic nanofibres.

In this study, synthesized nanotitania particles were electrospun into cross-linked fibres. It was evaluated by water contact angle test and exposed to the field test on the decomposition of polishing palm oil mill effluent (POME) solution by chemical oxygen demand (COD) test.

## 2. Materials and Methods

### 2.1. Materials and Suspensions

Commercially available titanium isopropoxide ($C_{12}H_{28}O_4Ti$ or ($Ti(OiPr)_4$)), ethanol 96%, polyvinylpyrollidone (PVP) 1.3 million MW, all from Sigma Aldrich were used in the present work.

8ml titanium isopropoxide ($Ti(OiPr)_4$) was mixed with 40ml ethanol and stirred in a clean, conical flask. The solution was added into 40ml cold distilled water of pH 2 by titration technique with continual stirring for 24 hours. The mixture was covered with foil and continued to be stirred for another hour. While 5.57g PVP and 40ml ethanol were mixed in a clean, lidded glass bottle and stirred continuing for an hour.

### 2.2. Electrospinning

In this experiment, 4ml of the $Ti(OiPr)_4$ solution was mixed with 4ml of the PVP solution to obtain the said stock solution. The solution was then placed inside a 10ml capacity syringe, the excess air bubbles were removed, and the syringe was placed in the syringe pump horizontally as shown in Figure 1. The high voltage clamp was then attached at the syringe needle, the pump turned on, then the power supply turned on. The formation of a stable jet was the first attempt with blank PVP solution via an adjustable knob on a variable scale with reading from a multimeter. Therefore the flow rate and voltage were varied to establish a range of electrospinning conditions for $Ti(OiPr)_4$ and PVP mixed solution. The power supply delivers at 18kV in this experiment, at flow rate of 0.5mlh-1 at a distance of 8cm from the needle tip to the collector.

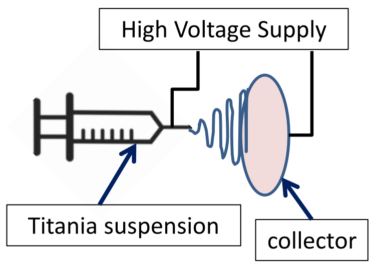


Fig. 1 Schematic diagram of an electrospinning apparatus setup

### 2.3. Heat Treatment and Characterization

The electrospun nanotitania fibres were collected on the alumina plate which was surrounding with the aluminium foil as the collector. The electrospun fibres with alumina were fired to 500$^{o}$C at 0.1$^{o}$Cmin$^{-1}$ with 1 hour soaking in air and cool naturally in the furnace (Superburn, Japan). Phase analysis of the initial electrospun fibres and fibres fired at 500$^{o}$C were analysed by X-ray diffraction (XRD) (Geiger-Flex, Rigaku Japan) of the samples was carried out under ambient conditions using Cu-K$\alpha$ as the radiation source at a scan speed of 0.5º per minute and a step scan of 0.02º. The morphology of the initial spun fibres and fibres fired at 500$^{o}$C were examined using a scanning electron microscope (SEM, Hitachi Japan).

For the water contact angle analysis, the coated alumina plate was first coat with a layer of oleic acid, a water drop was introduced by a syringe to the surface, using travelling microscope to take the image of the drop and the contact angle was analysed using "Big Drop Analysis" software. Then the coated glass plate was exposed to 1mWcm$^{-2}$ UV radiation system with 20W BLB Lamp for one hour. A second drop of water was dropped onto the surface, the contact angle was measured until the drop of water collapse of it spherical shape.

Fresh palm oil mill effluent (POME) solution was collected from palm oil mill for dilution until near polishing stage similar to the pond value prior to discharge. The alumina plate coated with fired electrospun nanotitania fibres was immersed in a beaker and cover with diluted POME solution. The test kit was exposed to sunlight of 40-70 Wm$^{-2}$ for 8 hours and the chemical oxygen demand (COD) of the said POME was determined.

## 3. Results and Discussion

### 3.1. Fibre and Thermal Analysis

SEM micrograph as shown in Figure 2 revealed the electrospun nanotitania fibres which are the mixture of from 50nm to 3$\mu$m fibres. These fibres were fused at the joint forming cross-linked like a web.

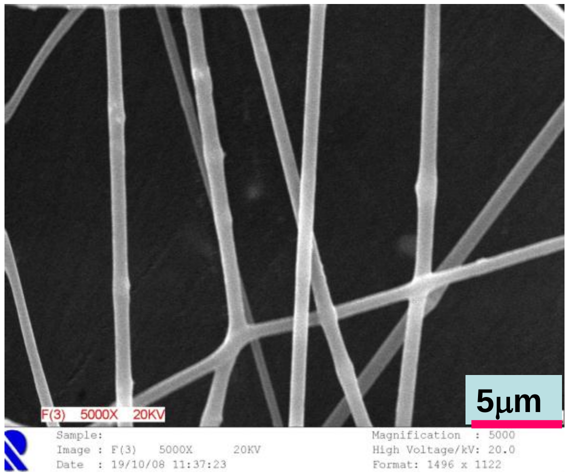


Fig. 2 SEM micrograph of nanotitania fibres producing by electrospinning at 18kV and distance of collector of 8cm at flow rate of $0.5 mlh^{-1}$

## 3.2. Heat Treatment and Phase Analysis

XRD analysis of the synthesized material revealed the amorphous phase of the initial material. The synthesized titania had transformed to anatase phase only at 500°C as shown in Figure 3.

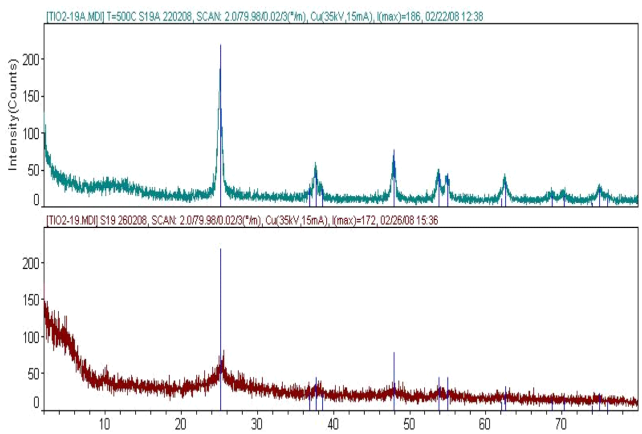


Fig. 3 XRD analysis had shown amorphous phase of dried powder (bottom) which transformed into anatase only after firing to 500°C (top)

## 3.3. Fibre and Micrograph Analysis

The fired electrospun nanotitania fibre had coagulated and formed irregular shape when it heat-treated to 500°C. The nanoparticles of the nanotitania had growth in size and had joined and formed the larger fibres that linked of the as shown in Figure 4.

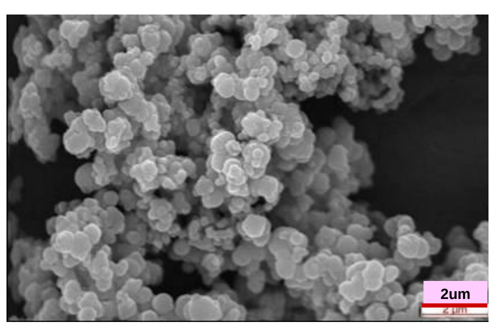


Fig. 4: SEM micrograph of electrospun nanotitania fibres displayed as linked nano-particles sintered at 500°C that shown the grain growth.

### 3.4. Performance Analysis

From Figure 5, the water contact angle graph had shown an initial contact angle of $70^o$ and it dropped down to about $10^o$ after 180min of $1mWcm^{-2}$ UV irradiation. From this performance analysis, the fired electrospun nanotitania fibres form as membrane coating was able to performance self-cleaning effect.

The chemical oxygen demand (COD) test had shown the reduction of COD in the POME under sunlight radiation. Some samples had shown the total removal of the COD in the POME. The results are tabulated in Table 1.

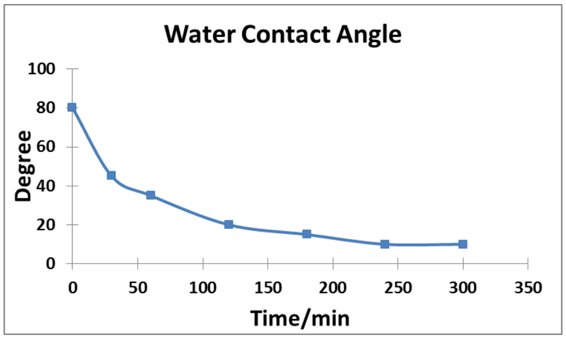


Fig. 5 The graph of the water contact angle conduct on the fired nanotitania electrospun fibre coating on the alumina plate under $1mWcm^{-2}$ UV irradiation.

TABLE I The result of the COD test before and after the 8h sunlight radiation with the present of fired electrospun nanotitania plate.

| COD Reading | POME solution (ppm) | | | |
|---|---|---|---|---|
| | **1** | **2** | **3** | **4** |
| initial | 145 | 236 | 284 | 120 |
| final | 5 | 13 | 12 | 0 |

## 4. Conclusions

The present work had shown that titania fibres were produced successfully from the titania suspension at 18kV at distance of 8cm of the electric field. Although majority of the fibres were in mirco, there are some nanofibres in the midst of the web. The SEM micrograph revealed nanotitania of the broken fibres sintered at $500^oC$ of anatase and grain growth with increase of temperature. The cross-linked fired electrospun nanotitania fibre formed cross-linked web-like structure may reduce the nano risk as compared to the nanoparticles. The contact angle test and chemical oxygen demand (COD) test had shown the present of radicals by fired electrospun nanotitania fibres. The fibres may decompose the palm oil mill effluent (POME) to the carbon dioxide and clean and odourless water.

## 5. Acknowledgements

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